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COMPARISON OF VISCOSITY AND MOLECULAR ARRANGEMENT IN TWENTY-TWO LIQUID OCTYL ALCOHOLS

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Abstract

A comparison is made between the x-ray diffraction halos of 22 octyl alcohols and their corresponding viscosities and an unmistakable correlation found. The assumptions are that the halos indicate periodicities, that the periodicities may be interpreted as structural in the "cybotactic" groups, and that the relative diffraction intensity of the halos computed by assuming crystal structure may be used to estimate roughly the perfection of the liquid groups. It thus is shown that there is a correlation between the coefficient of viscosity and the perfection of grouping in the direction of the length of the chain molecules. This corresponds with the reasonable view that the viscosity within the liquid groups is caused by longitudinal slippage. Moreover, since the groups at any instant occupy a large fraction of the volume of the liquid, this viscosity is an important part of that measured. This interpretation accounts for the negative temperature coefficient of the viscosity, since the size of the groups decrease with temperature. The experiments and conclusions are in accord with Andrade's theory of momentary "crystallization" and with Ornstein's theory of the formation of liquid crystal groups, yet it is to be noted that these theories deal with different aspects and not the entire phenomenon.

THE x-ray diffraction study by the author[1] of 22 octyl alcohols prepared in the laboratory of Professor E. Emmet Reid of Johns Hopkins University has made possible an interesting comparison of x-ray findings with the coefficient of viscosity of the same compounds. The comparsion as herewith presented, leads to the conclusion that this coefficient does have a dependence upon differences in the space arrangement (cybotaxis) of the molecules of liquid isomers as determined by x-ray data.

In the discussions in Nature[2] the differences in the origin of viscosity in liquids and gases is emphasized. The picture of the phenomenon in liquids as given by Andrade is that there is "a temporary union of molecules in contiguous layers, the duration of this union not exceeding the very brief time required for the molecules to acquire a common velocity of translation." This union takes place under the action of the molecular fields. "The general pic-

[1] Stewart, Phys. Rev. **35**, 726 (1930).

[2] By E. N. da C. Andrade, J. Frenkel, D. H. Black ,E. W. Madge and Ambrose Fleming in issue of April 12, 1930, and by E. C. Sheppard, March 29, 1930.

ture is one of the liquid "crystallizing" in minute patches." It is evident that Andrade's view borders closely upon what the author has chosen to call the "cybotactic" condition of the liquid. The x-ray evidence by diffraction in liquids, both in this laboratory[3] and elsewhere,[4] has accumulatively stressed the correctness of the view that there are in a liquid minute groups[5] or bundles of molecules in each one of which there is sufficient periodicity to account for the diffraction halos obtained.

It is further evident that this periodicity is not caused merely by the effect of the volume of the molecules,[6] but also by all the forces arising in the molecular fields as well. The importance of the molecular fields may be obtained from a general comparison of the liquid and crystalline state, for example in density, compressibility and latent heat of evaporation. But as a specific illustration of the necessity of the introduction of these fields may be cited the difference in diffraction halos of 3-ethyl pentane[3] and diethyl carbinol.[3] Both molecules are admittedly of practically the same size and shape, yet with the former only one halo of importance appears, whereas with the latter there are two very prominent. The additional halo in the diethyl carbinol is caused by a periodicity in the direction of the molecular lengths, one which does not appear at all in the nonpolar compound. Moreoever, the periodicities indicated by the other diffraction maxima are not of the same magnitude. But it is the purpose of this article not to submit the large amount of evidence favoring the existence of minute well-ordered temporary regions or groups of molecules in a liquid, but rather to point out an interesting comparison of the coefficient of viscosity with the perfection of these molecular groups as shown by x-rays. The results have been hitherto unpublished, chiefly because they have appeared more suggestive than conclusive. But the discussion of liquid viscosity already mentioned and the current interest in obtaining the appropriate basis for a theory of that phenomenon would seem to require that the experimental evidence connecting the cybotactic view with the nature of viscosity be submitted. To this will be added a brief theoretical discussion of the cybotactic view.

[3] See Stewart and collaborators, Morrow, Skinner, in a series of papers in Phys. Rev. from September 1927 to September 1931, and Spangler, Radiology **16,** 346 (1931).

[4] For reveiws of literature see, for example, Good, Physi a A ta, p. 305, 1930.

[5] It must be emphasized that the word "group" when describing molecular structure in a liquid, refers not to a minute crystal, to a region having a defined boundary, or to a permanent condition of the molecules involved. It refers to a region or spot of effective (at that instant) regularity of structure in a liquid. This condition of regularity of space arrangement fades off continuously into much less regularity. Hence there is no sharp boundary. These regions are very numerous occupying a large fraction of the total volume of liquid. A group does not retain its identity as determined by its constituent molecules. It is not a fragment of material, but it is a condition of position and potential energy which varies throughout the liquid. The existence of any group is temporary, yet the orderliness of the structure in more than one direction demands that its existence has a time duration.

[6] Debye in J. of Mathematics and Physics **4,** 133 (1925) and in Phys. Zeits. **28,** 315 (1927) has shown that even spherical atoms when occupying as much as one-half of the total volume, will produce an x-ray halo. Also Zernike and Prins, Zeits. f. Physik **41,** 184 (1927) emphasize the space effect.

Experimental

In order to make the discussion intelligible, the relative diffraction intensity curves for the 22 octyl alcohols are shown in Figs. 1, 2, and 3.[7] The angle θ is that read on the spectrometer. The radiation is essentially that of Mo$K\alpha$, but is not strictly monochromatic. Nevertheless its lack of homogeneity does not here lead to incorrect interpretations. Especially it should be remarked that any misleading effect of the continuous radiation is avoided by having a low voltage on the tube and by using thicknesses of samples that are less than the optimum for MoKα radiation. The original article may be consulted

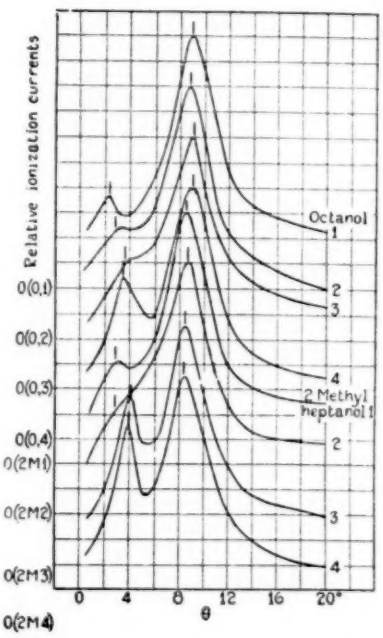

Fig. 1. X-ray diffraction; relative ionization currents of octyl alcohols.

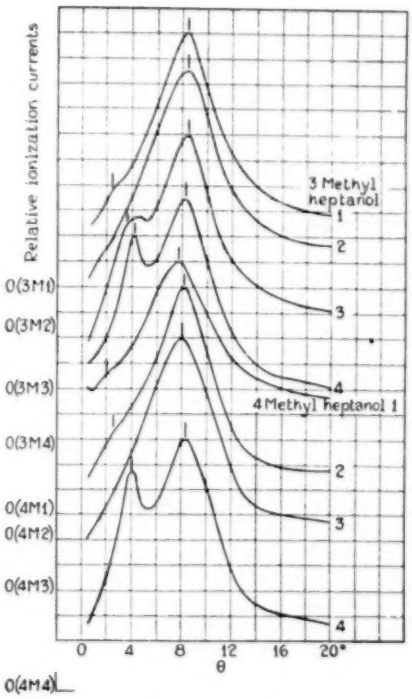

Fig. 2. X-ray diffraction; relative ionization currents of octyl alcohols

for the experimental details. It is assumed that these peaks indicate periodicity and that the most probable distance of separation of diffraction centers can be obtained by Bragg's law, $\lambda = 2d \sin \theta/2$. This assumption is warranted by the accepted view of crystal structure. The coherence in x-ray diffraction with crystals shows, by computation with Bragg's Law, the periodicities of the structure and in this interpretation both classical and quantum theories agree. Then for monochromatic radiation incident on a liquid, a band, instead of a line diffraction, may be interpreted as indicating not one periodicity but a number of them; as if one had powdered crystals with each set of planar separations varying over a small range in accord with a probability function. Some of the variation of periodicity, but much narrower in range,

[7] Stewart, Phys. Rev. **35**, 726–732 (1930).

may occur in the analogous single crystal also. The assumption of the correctness of Bragg's law for a liquid is thus based upon the straightforward conclusion that coherence indicates periodicity.

The periodicities obtained from the liquid are not sufficient to lead to a unique liquid structure. But it is in agreement with all the facts to assert that the molecules of n-alcohols, saturated normal fatty acids and n-paraffins[8] lie parallel in the so-called groups, with their long axes laterally equidistant and lying in two sets of parallel planes perpendicular to one another. This dimension is obtained from the major peak. On the other hand the position of the minor peak (not occurring with the paraffins) depends upon the length of the chain and is assumed to correspond to a periodicity having a direction or a component of a direction along the axes of the molecules. If the spacing of the molecules longitudinally is not orderly, permitting effective diffraction

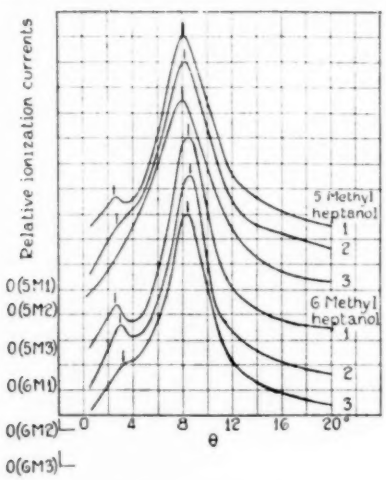

Fig. 3. X-ray diffraction; relative ionization currents of octyl alcohols.

centers to lie in parallel planes cutting the molecular axes, the minor peak will not be in evidence. These statements are consistent with all the facts and are discussed fully in the articles cited.

If one now considers the structure factor, F, of the molecules just as in the case of a crystal, it is easily seen[9] that the x-ray intensity from the lateral periodicity of these molecules will always be large and comparable with each other, while from the longitudinal periodicity the coherent scattering will be less and the variation among the compounds greater.

But as noted in x-ray diffraction experiments, these longitudinal periodicities appear (in chain compounds) only with polar molecules. The molecular field of a nonpolar chain compound is not sufficient to produce the longitudinal periodicity. One might thus expect that the slippage in the liquid groups may occur parallel to the molecular lengths and that there is a varia-

[8] Stewart and Morrow, Phys. Rev. **30,** 232 (1927); Morrow, Phys. Rev. **31,** 10 (1928); Stewart, Phys. Rev. **31,** 174 (1928).

[9] Spangler, Radiology **16,** 346 (1931).

tion in the intensities at the minor diffraction peaks not only because of structure factor but also because of the lack of perfection in the longitudinal periodicity.

One might thus anticipate that the viscosity would depend upon the perfection of the longitudinal periodicity, indeed, that the viscosity would increase with the perfection of grouping. This would be the case whether the groups occupied a large proportion of the volume or not. Clearly a comparison of the perfection of orderly longitudinal grouping with variation in viscosity would be advisable.

Degree of longitudinal periodicity in octyl alcohols compared with viscosity. The comparison just suggested must be of necessity crude, for one is not dealing with minute crystals wherein the structure factor of the molecules can be used with accuracy. Moreover, the structure of the liquid so-called groups is not definitely known. Reliance is placed merely upon a reasonable interpretation of diffraction curves.[9] The method of comparison is as follows.

TABLE I.

Compound	Heights of peaks	Computed relative heights	Col. 2–Col. 3 Ratio	Coefficient of viscosity
Octanol-1	11.0	24.9	0.433	0.204
Octanol-2	6.	12.4	.484	.218
Octanol-3	7.5	36.5	.206	.066
Octanol-4	27.2	69.0	.394	.154
2-methyl heptanol-1	11.0	49.5	.220	.083
2-methyl heptanol-2	6.0	40.0	.150	.091
2-methyl heptanol-3	28.0	104.	.270	.333
2-methyl heptanol-4	36.2	84.3	.430	.294
3-methyl heptanol-1	2.7	43.7	.062	.0361
3-methyl heptanol-2	0	29.1	0	.0311
3-methyl heptanol-3	16.5	140.	.118	.196
3-methyl heptanol-4	24.6	117.	.175	.042
4-methyl heptanol-1	1.0	53.2	.0188	.065
4-methyl heptanol-2	4.0	11.1	.364	.077
4-methyl heptanol-3	0.0	82.	0	.019
4-methyl heptanol-4	33.8	108.	.313	.322
5-methyl heptanol-1	6.0	13.6	.440	.137
5-methyl heptanol-2	4.0	4.46	.898	.047
5-methyl heptanol-3	0	84.5	0	.021
6-methyl heptanol-1	11.0	7.9	1.39	.227
6-methyl heptanol-2	17.8	3.92	4.54	.154
6-methyl heptanol-3	6.0	94.5	.0635	.026

In column two of Table I appear the relative heights of the secondary peaks as measured in Figs. 1, 2 and 3. In column 3 appear the relative heights these peaks should have if the diffraction occurred from powdered crystals having the structure mentioned. The computations for column 3 were made by Mr. Ross Spangler using the values of equivalent numbers of electrons as given by James and Brindley.[10] Column 3 then may be interpreted as indicating relative values of minor maxima in the diffraction curves which would occur if the groups were powdered crystals. Hence column 2 divided by column 3 would give a crude measure of the excellence or perfec-

[10] James and Brindley, Phil. Mag. **12**, 87 (1931).

tion of longitudinal periodicity which actually exists. This quotient is placed in column 4. In column 5 are given the observed coefficients of viscosity of these octyl alcohols as determined by Professor E. C. Bingham. The comparison is now made between column 4 and column 5 in Figs. 4 and 5. The values are plotted with change in molecular structure. With OH stationary and CH_3

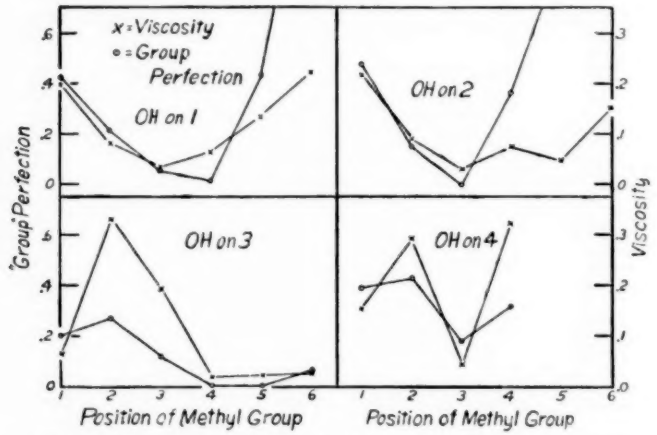

Fig. 4. Variation of "group" perfection and coefficient of viscosity.

attached as a branch to the different C atoms, the comparison is made in Fig. 4. It is to be noted that the range of the variables is large and therefore the correlation is striking. Only three compounds of the 22 in column four do not show a correlation. Similar comments may be made concerning Fig. 5 in which the position of the OH group is made the variable in the molecular

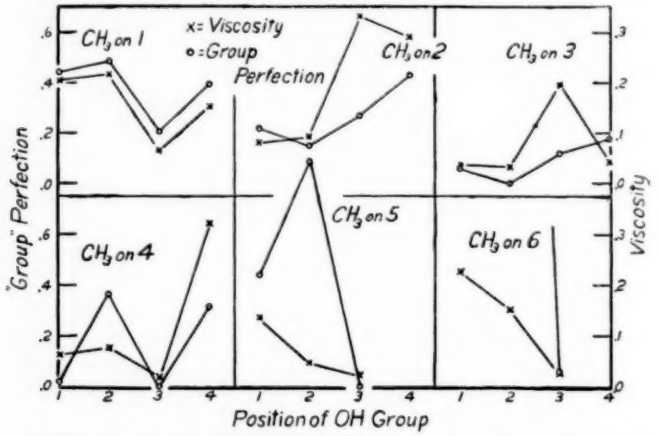

Fig. 5. Variation of "group" perfection and coefficient of viscosity.

structure. Incidentally, it may be pointed out that the three compounds with which the comparison is not favorable are those in which the molecule has OH near one end and CH_3 in a branch near the other. This indicates similar reasons for the disagreement, and the nature of the assumptions leaves ample room for such reasons. Speculations upon these disagreements are omitted

as having no purpose in this paper. That the correlation in Fig. 4 is noticeably better than in Fig. 5 is in harmony with the fact that in the former the polar group for any curve pair is stationary in the molecule. It should be pointed out that our assumptions take no consideration of the viscosity of the less regularly arranged molecules, which may depend on "shape." This is because, as mentioned below, these molecules are relatively few in number. Consequently the longitudinal slippage within the molecular groups is the chief factor in viscosity. From the foregoing evidence it now appears that the conditions producing the cybotactic condition in a liquid should be used as a basis for the consideration of the nature of liquid viscosity. This procedure is justified chiefly because of the evidence for cybotactic groups accumulated through x-ray diffraction experiments, but yet in part also because of the corroborative experiments here described.

The cybotactic view can be embodied in mathematical expressions only by very crude approximations, for the nature of the molecular fields is not understood. One such may be by the assumption of Andrade[11] as to a temporary union of molecules of one layer with another. This may be regarded as recognizing the existence of non-rigid somewhat orderly regions or groups in which, for example, molecules having a long axis will slip by one another in the direction of this axis. Andrade's theory has not been published so that it is impracticable to comment further on its conformity with the concept of groups advocated by the author.

A different approach to a theoretical consideration may be borrowed from Ornstein's[12] theory of liquid crystals. If the molecule is unsymmetrical, having a long axis, it is assumed that a molecule exerts a couple upon a neighboring one, the potential energy being proportional to the cosine of the angle between their axes and to a function of the distance of separation of the centers of mass of the molecules. Boltzmann's principle is applied. The theory finally leads to an expression which shows that the volume of the well-ordered regions decreases with an increase in temperature. From the experiments with x-rays it has become evident that, since the coherent diffraction with liquids is of the same order of magnitude[13] as that of the same mass in the form of crystal powder, the volume of the molecular groups is a large fraction of the total volume. Thus, if within the groups or well ordered regions the viscosity were greater than in the ungrouped molecules, the volume of the groups would be important in determining the measured value of the viscosity. An increase in temperature, decreasing this volume, would decrease the viscosity, which is in accord with experiments. In order to compute the effect, one would need to develop a theory for the dependence of viscosity upon the volume of the groups present when that volume is a large fraction of the whole.

The two theories are not contradictory, but refer to different aspects each without any claim of completeness. Andrade's theory emphasizes the effect of momentary group formation, which interferes with slippage. Ornstein's

[11] E. N. da C. Andrade, Nature, April 12, 1930.
[12] Ornstein, Zeits. f. Kristall. **79,** 90 (1931).
[13] Stewart, Phys. Rev. **37,** 9 (1931); See Fig. 1.

theory assumes a group which changes its size with temperature. In view of x-ray evidence concerning liquid diffraction it is reasonable to suppose that both conditions exist. It is significant that both causes lead to the correct sign of the change of viscosity with temperature and that both theories are in essential agreement with the cybotactic group view advocated by the author though as a matter of expediency they consider the conditions only in part.[14]

It is evident from the foregoing that a theory of viscosity which involves all the important aspects of the nature of a liquid is yet ahead, but that the theories of Andrade and of Ornstein are distinctly valuable. The cybotactic view would indicate the desirability of closer approximations in theory to the molecular fields existing in corresponding crystals. But until such fields are well understood the bases of theories proposed must of necessity be limited.

The reader is reminded that the correlation found between cybotactic group perfection and viscosity is presented because it seems opportune. The correlation is intrinsically not highly satisfactory. But the results do show an unmistakable relation, in spite of the various approximations that are of necessity made. This conclusion is however sufficient to emphasize the justification for the basis of viscosity theory similar to that given by Andrade. Not only does the temperature variation of viscosity point to an assumption of momentary union of molecules, but all x-ray diffraction experiments in liquids would urge the essential correctness of the assumption.

It is a pleasure to thank Professor E. Emmet Reid of Johns Hopkins University for the octyl alcohols used, Professor E. C. Bingham of Lafayette College for the viscosity data, and Dr. H. A. Zahl who, as a research assistant, took the x-ray data involved.

[14] There has just come to the attention of the author the earlier suggestions of Raman (Nature **111**, 532 and 600 (1923). He assumed two states of aggregation in the liquid "solid" and "vapor," and that the viscosity was proportional to the relative numbers of molecules in the two states. Raman's assumptions, while not those of the author, are closely similar. Raman's expression for the viscosity of a liquid is the same as Andrade, $\eta = Ae(b/T)$, where η is the viscosity coefficient, A and b are constants and T is the temperature. This formula agrees remarkably well with observed temperature variations. See also Iyer (Ind. J. of Physics, V Pt. IV, 371 (1930) for a discussion of the significance of A and b in Raman's suggestion.

THE BROWNIAN MOTION OF STRINGS AND ELASTIC RODS

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ABSTRACT

The method introduced by Ornstein is applied to calculate the Brownian-motion mean-square deviation for strings and for elastic rods, the surrounding medium being a gas. For the string, a varying tension and elastic binding at the ends are supposed, and a formula is obtained for the mean-square deviation of any point at time t, having started with a given deviation of that point; the result contains infinite series. This result is specialized to the string with fixed ends and constant tension. For the mid-point, and for a limited time interval, the series are summed; for $t\rightarrow\infty$, the result is given for all points, agreeing with that given by Ornstein for the mid-point. Elastic rods are treated similarly, and similar results are obtained. The effect of gravity, when the rod is vertical, is introduced by a simple and consequent preturbation method, and a formula is obtained for the mean-square deviation of the lower end; this agrees closely with Houdijk's experimental results. The time dependence given by the complete formula cannot yet be tested, for Houdijk gives only long-time mean values in his publication.

INTRODUCTION

1. Most of the theoretical work on Brownian motion has been concerned with only one degree of freedom, and it is the purpose of this paper to apply the method first introduced by Ornstein[1] to cases in which there are more (in fact, an infinite number) of degrees of freedom. The systems to be treated are: I. the stretched string, and II. the elastic rod. The first has been treated by Ornstein[2] and the second by Houdijk,[3] but in each case results were obtained only for $t\rightarrow\infty$ (that is, only "equipartition" values were found); our extensions will consist principally in giving the dependence of the mean-square deviation on the initial deviation and on the time, but we also treat a more general string before specializing to a particular case, and give a better treatment of the effect of gravity in the case of the rod.

In general our treatment will follow the lines of that used by Uhlenbeck and Ornstein[4] in their second (exact) calculation for the mean-square deviation of a harmonically-bound particle in Brownian motion, where they use the method of Ornstein. In this method one starts from the equation of motion and certain assumptions about the influence of the surrounding medium on the particle, and calculates directly the mean values sought, making use of certain properties of a canonical ensemble (a large number of similar, but

[1] L. S. Ornstein, K. Akad. Amsterdam Proc. **21**, 96 (1919), (in English).
[2] L. S. Ornstein, Zeits. f. Physik **41**, 848 (1927).
[3] A. Houdijk, Archives Neerlandaises des Sciences Exactes et Naturelles, Series III A, **11**, 212 (1928).
[4] G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930).

independent, particles) in evaluating constants which appear in the calculation. It will be of interest to record their result here, for it is of the same type as those which we shall obtain; with a slight change of notation, it is:

$$\overline{s^2}^{s_0} = \frac{kT}{m\omega^2} + \left(s_0^2 - \frac{kT}{m\omega^2}\right)e^{-\beta t}\left(\cos \omega_1 t + \frac{\beta}{2\omega_1}\sin \omega_1 t\right)^2 \tag{1}$$

where s is the displacement from equilibrium position, t the time, m the mass, and ω the (undamped) natural frequency in 2π sec., $\beta = f/m$, where f is the damping force per unit velocity, and $\omega_1^2 = \omega^2 - \beta^2/4$. This result, like all those obtained by this method, is not subject to the restriction (which must be imposed on results obtained by certain other methods) that t must be large compared to β^{-1}, hence the term "exact."

Now it is well known that the vibrating string may be treated by means of its normal vibrations, and that each normal vibration obeys the equation of the harmonic oscillator; also, we shall show the same to be true of the rod. Thus we may, so to say, consider in each case the system to be an assembly of damped harmonic oscillators, each having for its frequency that of the corresponding normal vibration. The deviation of any point will then be determined by the displacements of all the component "oscillators," and similarly for the squared displacement, velocity, etc. Thus one can foresee that the treatment will not be essentially different from that for the harmonic oscillator itself, the additional elements necessary being: (1) the deduction from our assumptions (about the influence of the surrounding medium on the system) of results which will take the places of analogous assumptions for the individual "oscillators," (2) the treatment of the sums which result, and (3) a certain averaging process which is more complicated than that necessary for a single oscillator, and which will arise when we wish to make the known initial conditions apply to only one point of the string or rod.

I. The Brownian Motion of a Homogeneous String

2. We consider the Brownian motion of a homogeneous string (i.e., one with constant linear density ρ) of length L, surrounded by a gas. The string is bound elastically at its ends and is under a tension $\tau(x)$ which may vary with the distance x along it. The equation of motion of the string is:

$$\rho\frac{\partial^2 s}{\partial t^2} + f\frac{\partial s}{\partial t} = \frac{\partial}{\partial x}\left(\tau\frac{\partial s}{\partial x}\right) + F(x, t)$$

where f is the friction coefficient and $F(x,t)$ is the fluctuating force. This may be written:

$$\frac{\partial^2 s}{\partial t^2} + \beta\frac{\partial s}{\partial t} = p'\frac{\partial s}{\partial x} + p\frac{\partial^2 s}{\partial x^2} + A(x, t) \tag{2}$$

where $\beta = f/\rho$, $p = \tau/\rho$, $A = F/\rho$. The conditions to be satisfied at the ends are:

$$\begin{aligned} h_0 s(0, t) - \left(\frac{\partial s}{\partial x}\right)_{x=0} &= 0 \\ - h_L s(L, t) - \left(\frac{\partial s}{\partial x}\right)_{x=L} &= 0 \end{aligned} \tag{3}$$

where h_0 and h_L are the ratios of elastic constant of binding to tension at the two ends.

The assumptions which we make for this case are the natural generalizations of Ornstein's assumptions for the simpler cases, namely that the influence of the surrounding gas may be split up into two parts; (1) a systematic frictional force, $-f(\partial s/\partial t)$ per unit length, where f is a constant depending on the nature of the gas and its pressure, and (2) a fluctuating force, $F(x,t)$ per unit length, about which we make further assumptions in terms of $A(x,t)$:

$$\overline{A(x, t)} = 0 \tag{4}$$

$$\overline{A(x_1, t_1)A(x_2, t_2)} = \phi(x_1 - x_2, t_1 - t_2) \tag{5}$$

where $\phi(x,t)$ is even in both x and t and has a sharp maximum at (0,0). The mean is taken over a subensemble, each member of which started at $t=0$ with a given shape and distribution of velocity along it.

If we consider the homogeneous equation obtained by omitting the last term from (2), the usual treatment by separation of variables gives rise to two differential equations, of which the "space" one is a slightly-specialized case of the Sturm-Liouville equation. This equation, together with the boundary conditions, defines in the usual way the orthogonal eigenfunctions X_n, which we shall assume normalized, and which satisfy the following differential equation and boundary conditions:

$$pX_n'' + p'X_n' + \lambda_n X_n = 0 \tag{6}$$

and

$$\begin{aligned} h_0 X_n(0) - X_n'(0) &= 0 \\ - h_L X_n(L) - X_n'(L) &= 0 \end{aligned} \tag{7}$$

where λ_n is the corresponding eigenvalue.

We now return to Eq. (2), and expand $s(x,t)$ and $A(x,t)$ each in a series of eigenfunctions with coefficients which depend on the time:

$$s(x, t) = \sum_{n=1}^{\infty} S_n(t) X_n(x) \tag{8}$$

$$A(x, t) = \sum_{n=1}^{\infty} A_n(t) X_n(x). \tag{9}$$

Substituting these expansions into (2), equating to zero each term of the

sum which results if we transfer all terms to the left-hand member, and using (6), we obtain as the equation for $S_n(t)$:

$$S_n'' + \beta S_n' + \lambda_n S_n = A_n(t). \tag{10}$$

We can write down at once the general solution of this, which is:

$$S_n(t) = \left[\frac{\beta S_n(0) + 2S_n'(0)}{2\omega_n} \sin \omega_n t + S_n(0) \cos \omega_n t\right] e^{-\beta t/2} + \frac{1}{\omega_n}\int_0^t A_n(v) e^{-\beta(t-v)/2} \sin \omega_n(t-v)dv \tag{11}$$

where

$$\omega_n^2 = \lambda_n - \tfrac{1}{4}\beta^2 \tag{12}$$

and we restrict ourselves to the case in which all the eigenvibrations are periodic by assuming

$$\lambda_n > \tfrac{1}{4}\beta^2.$$

$S_n(0)$ and $S_n'(0)$ are clearly the n-th coefficients of the expansions of the initial displacement and velocity, respectively.

3. As a preliminary step, which will furnish us with results to be needed later, we shall calculate the mean-square deviation of any point for simple initial conditions, supposing that at $t=0$ the string is at rest in its equilibrium position. This means that $S_n(0) = S_n'(0) = 0$, and denoting by $\overline{S^2}^0$ the mean-square deviation for these initial conditions, we obtain

$$\overline{s^2}^0 = \sum_1^\infty \frac{1}{\omega_n^2} \overline{I_n^2} X_n^2(x) \tag{13}$$

where

$$I_n = \int_0^t A_n(v) e^{-\beta(t-v)/2} \sin \omega_n(t-v)dv \tag{14}$$

because the double sum which results directly from (8) is reduced to a single sum by the fact (proved in Note 1, on the basis of assumption (5)) that $\overline{I_n I_m} = 0$ if $m \neq n$; this has the meaning that the different eigenvibrations are uncorrelated, in so far as they arise solely from the fluctuating force.

For $\overline{I_n^2}$ we get an integral similar to those occurring in the paper of Uhlenbeck and Ornstein;[4] using the results of Note 1, we find

$$\overline{I_n^2(t)} = \frac{\alpha_n}{2\beta}(1 - e^{-\beta t}) - \frac{\gamma_n}{4\lambda_n}\left\{\tfrac{1}{2}\beta + e^{-\beta t}(\omega_n \sin 2\omega_n t - \tfrac{1}{2}\beta \cos 2\omega_n t)\right\} \tag{15}$$

where

$$\gamma_n = \int_{-\infty}^{+\infty} \psi_n(v)dv, \quad \alpha_n = \int_{-\infty}^{+\infty} \psi_n(v) \cos \omega_n v dv,$$
$$\psi_n(v - w) = \overline{A_n(v)A_n(w)};$$

thus

$$\overline{I_n^2(\infty)} = \frac{\alpha_n}{2\beta} - \frac{\gamma_n \beta}{8\lambda_n}. \tag{16}$$

To determine the constants α_n and γ_n, we make use of the same devices as were used by Uhlenbeck and Ornstein for the harmonic oscillator; that is, we equate the mean potential energy of each eigenvibration (the mean being taken over a canonical ensemble) to $kT/2$, and the correlation between deviation and velocity to zero. In this way we obtain the result:

$$\alpha_n = \gamma_n = \frac{2\beta kT}{\rho}. \tag{17}$$

The calculations are given in Note 2.

One might fear that the assigning of the potential (and kinetic) energy $kT/2$ to each eigenvibration would give rise to convergence difficulties, since it makes the total energy of the system infinite, but this is not the case. We inquire only about the mean-square deviation, and the series which result are all amply convergent. However, there is a further point which may seem strange, namely that we found α_n and γ_n to be equal and independent of n. Their equality (which follows from only our initial assumptions and the lack of correlation between deviation and velocity, the use of the equipartition energy not being involved) would indicate that the correlation function, $\phi(x,t)$, is infinitely sharp in both x and t, and this one cannot believe.[5] However this difficulty becomes serious only at high frequencies, and seems to indicate that our assumptions must not be used where one is concerned with times that are too small, say of the order of magnitude of the time between successive molecular impacts on any small length considered. However, this limitation is much less stringent than that which had to be imposed on certain earlier work, where the results were not valid for times of the order of magnitude of β^{-1} or less, and on account of the convergence properties of our solutions, it brings in no difficulties here. The independence of n is to be understood in a similar way.

By substitution of (19), (17) becomes:

$$\overline{I_n}^2 = \frac{\omega_n{}^2 kT}{\rho\lambda_n} - \frac{kT}{2\rho\lambda_n} e^{-\beta t}\left\{\frac{4\lambda_n + \beta^2}{2\beta} + \omega_n \sin 2\omega_n t - \tfrac{1}{2}\beta \cos 2\omega_n t\right\} \tag{18}$$

and we obtain from (15):

$$\overline{s^2(x,t)}^0 = \frac{kT}{\rho} \sum_1^\infty \frac{X_n{}^2(x)}{\lambda_n}\left\{1 - \frac{\beta}{2\omega_n{}^2} e^{-\beta t}\left(\frac{4\lambda_n + \beta^2}{2\beta} + \omega_n \sin 2\omega_n t + \tfrac{1}{2}\beta \cos 2\omega_n t\right)\right\}. \tag{19}$$

Taking the limit of this expression for $t \to \infty$, we obtain for a canonical ensemble:

$$\overline{s^2} = \frac{kT}{\rho} F(x) \tag{20}$$

where:

$$F(x) = \sum_1^\infty \frac{X_n{}^2(x)}{\lambda_n}. \tag{21}$$

[5] Quite analogous questions must be raised in the case of the harmonic oscillator.

4. We are now ready to calculate a quantity which is more easily measured than that given by (21), namely the mean-square deviation of a given point of the string, after having started at $t=0$ with a given initial deflection of that point. Let this given value be C, so that:

$$s(x, 0) = C$$

for the particular value of x under consideration; this value will be taken to be the same throughout this discussion, so that in this section x is a constant. this means that:

$$\sum_1^\infty X_n(x)S_n(0) = C \tag{22}$$

and it is the value of this linear combination of the $S_n(0)$ which is to be given; otherwise we are to average over a canonical ensemble. That is to say, we consider a canonical ensemble of strings and, fixing on some particular numbers for x and C, pick out of it at $t=0$ a subensemble, all members of which have the deflections of the x-points equal to C. We then follow these strings in their motions, and it is the squared deflections of their x-points, averaged over this subensemble, which we wish to calculate.

To this end one may first calculate $\overline{s^2}^{s_0 u_0}$, which is the mean-square deviation of a subensemble, each member of which has initially the same given shape and velocity distribution along it. This means that for each member, $S_n(0)$ and $S_n'(0)$ are the same; the difference in behavior of the different members arises only out of the fact that the fluctuating force, $F(x,t)$ varies from member to member. Next one calculates $\overline{\overline{s^2}}^{s_0}$, which is the mean-square deviation of a subensemble, each member of which has initially the same shape, and hence the same set of $S_n(0)$, no attention being paid to velocities. This is to be obtained by averaging $\overline{s^2}^{s_0 u_0}$ over the $S_n'(0)$, using the facts that $\overline{S_n'(0)}=0$ (which follows from the lack of correlation between displacement and velocity in a canonical-ensemble) and that $\overline{S_n'^2(0)}$ has the value corresponding to equipartition of kinetic energy. The final result sought is to be obtained by averaging $\overline{\overline{s^2}}^{s_0}$ over the $S_n(0)$ with the restriction (22).

We find:

$$\overline{\overline{s^2}}^{s_0} = \sum_{n=1}^\infty \sum_{m=1}^\infty X_n X_m \left\{ S_n(0)S_m(0)B_nB_m + \delta_{nm}\frac{kT}{\rho\lambda_n}(1 - B_n^2) \right\} \tag{23}$$

where

$$B_n(t) = e^{-\beta t/2}\left(\frac{\beta}{2\omega_n}\sin\omega_n t + \cos\omega_n t\right). \tag{24}$$

Now

$$\overline{\overline{s^2}}^{c} = \frac{\int_c \cdots \int \overline{\overline{s^2}}^{s_0} \exp(-V/kT)dS_1(0)dS_2(0)\cdots}{\int_c \cdots \int \exp(-V/kT)dS_1(0)dS_2(0)\cdots}$$

where V is the potential energy given in Note 2, and the C written under the integral-signs (an infinite number of them are implied) means that the integrations are to be performed with the condition (22). Using (23) and interchanging summations and integrations we obtain a result which contains the quotient of two integrals. This quotient is evaluated in Note 3, and using this, we obtain as the final result:

$$\frac{\overline{c}}{s^2} = \frac{kT}{\rho}F(x) + \left[C^2 - \frac{kT}{\rho}F(x)\right]e^{-\beta t}\left[\frac{1}{F(x)}\frac{\partial G}{\partial t} + \frac{\beta}{2F(x)}G\right]^2 \tag{25}$$

where

$$G(x, t) = \sum_{n=1}^{\infty} \frac{X_n^2 \sin \omega_n t}{\omega_n \lambda_n}. \tag{26}$$

This is in complete correspondence with Eq. (1) for the harmonic oscillator, in which $(\sin \omega_1 t)/\omega_1$ plays the same part as $G(x,t)/F(x)$, and $1/\omega^2$ corresponds to $F(x)$. It is interesting to observe (as can be shown to follow at once from the form of (25)) that this mean-square deviation never crosses the equipartition value, and further, that the curves corresponding to a given value of β, but to different values of C, differ only in scale, when referred to the equipartition line. These statements are true also for the harmonic oscillator.

5. As an example we consider the string with fixed ends and constant tension. For this case, we find:

$$F(x) = \frac{2L}{a^2\pi^2}\sum_{1}^{\infty}\frac{\sin^2 n\pi x/L}{n^2} = \frac{L}{a^2}\left(\frac{x}{L} - \frac{x^2}{L^2}\right)$$

where

$$a = \left(\frac{\tau}{m}\right)^{1/2} = \text{wave velocity}.$$

This gives us:[6]

$$\overline{s^2(x)} = \frac{kTL}{\tau}\left(\frac{x}{L} - \frac{x^2}{L^2}\right). \tag{27}$$

The other result to be specialized is (25). In this there appears, in addition to $F(x)$, the function $G(x,t)$ and its time derivative. The corresponding series contain both x and t as variables, and in this general form we have not been able to sum them. However, if we restrict our attention to the mid-point of the string, we can further simplify matters, for we shall show in Note 4 that for the interval $0 \leqq t \leqq L/a$, we may write:

$$G(L/2, t) = \frac{2L}{a^2\pi^2}\sum_{n\,\text{odd}}\frac{\sin\,(n^2a^2\pi^2/L^2 - \beta^2/4)^{1/2}t}{n^2(n^2a^2\pi^2/L^2 - \beta^2/4)^{1/2}}$$

$$= \frac{L}{2a^2}\left\{\sinh\,(\beta t/2) - \frac{2at}{L}I_1(\beta t/2)\right\}$$

$$\frac{dG(L/2, t)}{dt} = \frac{L}{4a^2}\left\{\cosh\,(\beta t/2) - \frac{2at}{L}I_0(\beta t/2)\right\}$$

[6] For the mid-point this gives the value $kTL/4\tau$, which has been given by Ornstein, reference 2.

where

$$I_n(z) = i^{-n}J_n(iz)$$

and $J_n(x)$ is the Bessel function of order n. Using these expressions and reducing, (25) becomes:

$$\overline{\overline{S^2(L/2,t)}}^c = \frac{kTL}{4\tau} + \left[C^2 - \frac{kTL}{4\tau}\right]\left\{1 - \frac{2at}{L}e^{-\beta t/2}[I_0(\beta t/2) + I_1(\beta t/2)]\right\}^2 \quad (28)$$

for:

$$0 \leqq t \leqq L/a.$$

In Fig. 1 we have plotted some curves showing how $\overline{\overline{s^2}}^c$ depends on the time. For these we have taken $a = L = 1$, $\beta = 1,2,3,4$, and $C^2 = 0$ and $= 3kT/4\tau$. For $0 \leqq t \leqq 1$ (28) was used; for later times it was necessary to use the series themselves, although it was found possible to replace β by zero in these

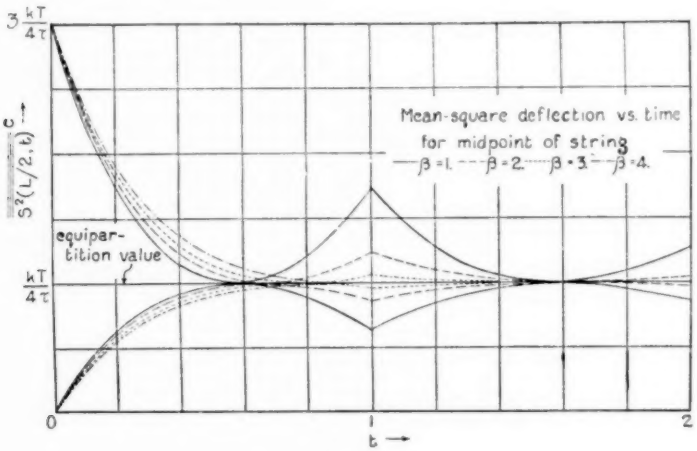

Fig. 1.

series without introducing too great an error. The apparent cusps in the curves at $t = 1$ are curious; they are not in fact quite cusps if β is different from zero, but the difference is not apparent to the eye with the scale used.

II. The Brownian Motion of an Elastic Rod

6. We shall first treat, in the same manner as for the string, the problem of the Brownian motion of an elastic rod which has one end clamped and the other free, and later consider the effect of gravity. We take these end conditions because they are the ones most easily realized in experiments; the problem could as readily be carried through for any other combination of the usual conditions.

The equation of motion of an elastic rod under no forces is given by Rayleigh[7] as:

[7] Lord Rayleigh, Theory of Sound (London. Macmillan, 1894), vol. 1, p. 258.

$$\frac{\partial^2 S}{\partial t^2} + \frac{r^2 E}{4d}\frac{\partial^4 s}{\partial x^4} - \frac{r^2}{4}\frac{\partial^4 s}{\partial x^2 \partial t^2} = 0$$

where E = Young's modulus, r = radius of cross-section (assumed circular and constant), d = volume-density; other symbols are as for the string. The third term of the first member arises out of the kinetic energy of rotation of the cross-sectional laminae; it is neglected by Rayleigh in his further treatment, and we shall do likewise. Adding the damping and accidental-force terms, we obtain:

$$\frac{\partial^2 s}{\partial t^2} + \beta\frac{\partial s}{\partial t} + \frac{r^2 E}{4d}\frac{\partial^4 s}{\partial x^4} = A(x, t). \tag{29}$$

Taking the origin at the clamped end, and the end conditions (also given by Rayleigh) are:

$$\begin{aligned} s = 0, \quad \frac{\partial s}{\partial x} = 0 \quad &\text{for } x = 0 \\ \frac{\partial^2 s}{\partial x^2} = 0, \quad \frac{\partial^3 s}{\partial x^3} = 0 \quad &\text{for } x = L \end{aligned} \tag{30}$$

We make the same assumptions about $A(x, t)$ as for the string.

If we consider the homogeneous equation obtained by replacing the second member of (29) by zero and separate the variables as usual, the resulting "space" equation is:

$$\frac{d^4 X}{dx^4} = \frac{4\lambda d}{r^2 E} X$$

where λ is the separation parameter. The situation is the same as that obtaining for the Sturm-Liouville equation for, as Rayleigh shows, this equation, together with the boundary conditions arising out of (30), gives rise to a complete set of orthogonal eigenfunctions:

$$X_n = b_n[a_n(\cos m_n x/L - \cosh m_n x/L) + (\sin m_n x/L - \sinh m_n x/L)] \tag{31}$$

where m_n is the nth positive root of the equation:

$$\cos m \cdot \cosh m + 1 = 0 \tag{32}$$

$$a_n = \frac{\cos m_n + \cosh m_n}{\sin m_n - \sinh m_n} \tag{33}$$

$$\lambda_n = \frac{r^2 E m_n^4}{4dL^4} \tag{34}$$

and the coefficients b_n are chosen for normalization. Rayleigh discusses the roots of (32) and calculates the first few, giving formulas from which the rest can be found. In addition he shows that:

$$\sum_{n=1}^{\infty} \frac{1}{m_n^4} = \frac{1}{12} \tag{35}$$

and

$$X_n^2(L) = \frac{4}{L}. \tag{36}$$

We shall have occasion to use these results.

Returning to Eq. (29), we proceed just as for the string and expand $s(x, t)$ and $A(x, t)$ each in a series of eigenfunctions with coefficients which depend on the time; in the same way as before, we obtain Eq. (10) for $S_n(t)$, so that Eqs. (8)—(12) of article 2 apply as well as to this case as to the string.

7. The calculation of the mean-square deviation of any point, supposing that at $t = o$ the rod is at rest in its equilibrium position, follows here exactly as for the string; we may take all the equations of that article to apply to the present case. To obtain Eq. (17), however, we must use for the potential energy:

$$V = \frac{\pi r^4 E}{8} \int_0^L \frac{ds}{R^2}$$

where R is the radius of curvature of the rod at the point. In view of the approximate straightness we may replace this by:

$$V = \frac{\pi r^4 E}{8} \int_0^L \left(\frac{\partial^2 s}{\partial x^2}\right)^2 dx.$$

Using this, together with the differential equation and boundary conditions for the eigenfunctions, we again arrive at (*B*) of Note 2. The corresponding expression for the potential energy of the nth eigenvibration becomes, on using (36):

$$V_n = \frac{\pi r^4 E}{8L^4} m_n^4 S_n^2. \tag{37}$$

The further calculations are identical, and we again arrive at (17) where now $\rho = \pi r^2 d$. Hence results (18), (19) and (20) are valid for this case also; substituting for λ_n by (34) in (20) we obtain for the canonical-ensemble mean-square deviation of any point x:

$$\overline{s^2} = \frac{4L^4 kT}{\pi r^4 E} \sum_{n=1}^{\infty} \frac{X_n^2(x)}{m_n^4} \tag{38}$$

and for the free end, using (36) and (35) we obtain the result already given by Houdijk[3]:

$$\overline{s^2} = \frac{4L^3 kT}{3\pi r^4 E}. \tag{39}$$

The calculations of article 4 for the string, in which we found an expression (given by Eq. (25)) for the mean-square deviation of a given point x, after having started at $t=o$ with a given initial deviation C of that point, apply just as well to the rod. The general result becomes especially simple for the free end because the series converge quite strongly on account of the rapid increase of m_n. Taking only the first terms, and using *12* for m_1^4 instead of *12.4* (since this makes the value at $t=o$ strictly correct), we obtain:

$$\overline{\overline{s^2(L,t)}}^c \cong \frac{4L^3kT}{3\pi r^4E} + \left(C^2 - \frac{4L^3kT}{3\pi r^4E}\right)e^{-\beta t}\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right)^2 \tag{40}$$

where:

$$\omega_1^2 = \lambda_1 - \tfrac{1}{4}\beta^2 = \frac{3r^2E}{dL^4} - \tfrac{1}{4}\beta^2.$$

8. Houdijk[3] has observed the Brownian motion of the lower ends of thin filaments which were clamped vertically at their upper ends and were otherwise free, the surrounding medium being air. It is necessary in this case to take into account the effect of gravity, and we shall now modify the foregoing treatment in this regard. We shall assume that a rod under gravity executes the same eigenvibrations as without it and that their amplitudes will bear approximately the same ratios to each other, the effect of gravity being to increase the potential energy associated with each. We shall restrict our attention to the free (lower) end, and we may with good approximation assume that the form of the rod is given by the first eigenfunction.

To obtain the contribution, ΔV_1, of gravitation to the potential energy, we treat the rod as a string under the tension $\rho g(L-x)$, where we again use ρ for the linear density; thus we have:

$$\Delta V_1 = \frac{\rho g}{2}\int_0^L (L-x)\left(\frac{\partial s}{\partial x}\right)^2 dx; \tag{41}$$

this is completely equivalent to multiplying the total mass by the distance through which its center of gravity is raised in bending it to a given shape. In accordance with the approximation mentioned above, we write:

$$s = S_1(t)X_1(x)$$

Substituting in (41), using the expression (31) for $X_1(x)$, and using the fact that to our present approximation, $s^2(L,t) = 4/L \cdot S_1^2(t)$ we obtain:

$$\Delta V_1 = \frac{0.98\rho g}{8}s^2(L,t)$$

To the same approximation,

$$V_1 = \frac{\pi r^4 E}{32L^3}m_1^4 s^2(L,t)$$

so that

$$V_1 + \Delta V_1 = \frac{\pi r^4 E m_1^4 + 3\cdot 96\rho g L^3}{32L^3}\, s^2(L, t) = \frac{kT}{2}.$$

Subsituting $\pi r^2 d$ for ρ and 12 for m_1^4, we obtain:

$$\overline{s^2(L)} = kT\,\frac{4L^3}{3\pi r^4 E + 0.98\pi r^2 d g L^3}. \tag{42}$$

This formula is practically identical with the one given by Houdijk, the only difference being that he has the number 1 where we have 0.98, and this difference is much too small to be significant in the comparison with experimental results. We have given the above derivation because we believe it to be more consequent then Houdijk's. His observations agree very well with the values predicted by this formula. The closeness of agreement is indicated by the fact that he uses it to determine Avogadro's number, N, (substituting R/N for k) from his observations, finding as the average of ten determinations the value 6.36×10^{23}, which differs from the accepted value of 6.06×10^{23} by only 5 percent.

Concerning the dependence of the mean-square deviation on the initial conditions and the time, to adapt formula (40) to this case we need only replace the equipartition value given there by the second member of (42). This formula cannot yet be tested, for Houdijk gives only limiting values in his publication.

Notes

Note 1. We are to investigate the quantity $\overline{I_n I_m}$; it is clear that if we write it as a double integral, it will contain under the integral signs the quantity $\overline{A_n(v)A_m(w)}$, and by using (10) we obtain for this:

$$\overline{A_n(v)A_m(w)} = \int_0^L \int_0^L \overline{A(x, v)A(y, w)}X_n(x)X_m(y)dxdy.$$

Now let $x-y=u$ and $y=z$; using (5),

$$\overline{A_n(v)A_m(w)} = \int_0^L dz \int_{-\infty}^{+\infty} \phi(u, v-w)X_n(u+z)X_m(z)du.$$

But $\phi(u, v-w)$ differs from zero only for u very little different from zero, hence we replace $X_n(u+z)$ by $X_n(z)$ in the integrand, and by using the orthogonality property we obtain.

$$\overline{A_n(v)A_m(w)} = \delta_{nm}\psi_n(v-w)$$

where

$$\psi_n(v-w) = \int_{-\infty}^{+\infty} \phi(u, v-w)du$$

So that

$$\overline{I_n I_m} = 0 \quad \text{for} \quad n \neq m.$$

This procedure is of course not rigorous unless $\phi(u, v-w)$ is infinitely "sharp" in u, which we have not assumed.

For the string with fixed ends and constant tension, however, the eigenfunctions are sines, and in this case we may improve the argument. We have:

$$\overline{A_n(v)A_m(w)} = \frac{2}{L}\int_0^L dz \int_{-\infty}^{+\infty} \phi(u, v-w)\left[\sin\frac{n\pi u}{L}\cos\frac{n\pi z}{L} + \cos\frac{n\pi u}{L}\sin\frac{n\pi z}{L}\right]\sin\frac{m\pi z}{L}du.$$

When integrated, the first term of this gives zero because in the integration over u the integrand is an odd function, and the second term gives zero in the integration over z if $n \neq m$ because of the orthogonality of the sines. If $n=m$, however, we obtain:

$$\overline{A_n(v)A_m(w)} = \int_{-\infty}^{+\infty} \phi(u, v-w) \cos\frac{n\pi u}{L}\, du = \psi_n(v-w).$$

It is clear from this that for this case, ψ_n should be expected to depend on n, in that it will be diminished for very high values of n if ϕ is not infinitely sharp in its dependence on u, and therefore we have allowed for this also in the general case.

Note 2. We are to determine the constants α_n and γ_n. The potential energy of the system, which includes the potential energy of the binding at the ends is:

$$V = \tfrac{1}{2}\rho\left\{\int_0^L p(x)\left(\frac{\partial s}{\partial x}\right)^2 dx + h_0 p(0)s^2(0,t) + h_L p(L)s^2(L,t)\right\}.$$

When we substitute (8) into this, interchange summations and integration, and integrate by parts (using (7) and the orthogonality property), we find:

$$V = \tfrac{1}{2}\rho \sum_{n=1}^{\infty} \lambda_n S_n^2 \tag{A}$$

or

$$V_n = \frac{\rho\lambda_n}{2} S_n^2$$

where V_n is the potential energy of the n-th eigenvibration. In a similar manner, although much more simply, we find for the kinetic energy:

$$K = \tfrac{1}{2}\rho \sum S_n'^2$$
$$K_n = \tfrac{1}{2}\rho S_n'^2.$$

For $t \to \infty$, the subensemble which started at $t=0$ from rest and equilibrium position will become a canonical ensemble; thus:

$$\lim_{t\to\infty} \overline{V_n}^0 = \frac{\rho\lambda_n}{2}\overline{S_n^2(\infty)}^0 = \frac{\rho\lambda_n}{2\omega_n^2}\overline{I_n^2(\infty)} = \frac{kT}{2}.$$

Substituting (16) into this, we obtain the relation:

$$4\alpha_n\lambda_n - \gamma_n\beta^2 = \frac{8\omega_n^2\beta kT}{\rho}. \tag{B}$$

If we similarly equate the kinetic energy of the n-th eigenvibration to $kT/2$ we obtain, not another relation, but the same one again, as might have been expected from the results for the harmonic oscillator. To confirm this statement, one must calculate $S_n'^2(\infty)$ in the same way that we have calculated $S_n^2(\infty)$.

To get another relation we make use of the fact that in a canonical ensemble of strings there will be no correlation between the displacement and the velocity for any point. Thus, writing $u = ds/dt$:

$$\overline{su}^0 = \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \frac{1}{\omega_n\omega_m}\overline{I_nJ_m}X_nX_m$$

where J_m is an integral similar to I_m. Now it is clear that $\overline{I_nJ_m}$ will contain under the integral signs the quantity $\overline{A_n(v)A_m(w)}$, and we have shown that this vanishes unless $m=n$. Therefore, the double sum reduces to a single sum. Our requirement that $\operatorname{Lim}_{t\to\infty} \overline{su}^0 = 0$ gives the result $\alpha_n = \gamma_n$ and putting this into (B),

$$\alpha_n = \gamma_n = \frac{2\beta kT}{\rho}.$$

Note 3. The ratio of integrals to be calculated is.

$$L_{nm} = \frac{\int \cdots \int_C S_n(0)S_m(0) \exp\left\{ -\rho \sum_1^\infty \lambda_i S_i^2(0)/2kT \right\} dS_1(0)dS_2(0) \cdots}{\int \cdots \int_C \exp\left[-\rho \sum_1^\infty \lambda_i S_i^2(0)/2kT \right] dS_1(0)dS_2(0) \cdots}$$

where the integration are to be carried out with the condition:

$$\sum_{n=1}^\infty X_n S_n(0) = C.$$

Let us first take the integrals to be only N-tuple, and the summations correspondingly to go only from 1 to N, afterward taking the limit for $N \to \infty$. Now introduce the new variables:

$$y_n = S_n(0)\left(\frac{\rho\lambda_n}{2kT}\right)^{1/2}.$$

The Jacobian of the transformation of course does not matter, being the same in the numerator and denominator; this gives us:

$$L_{nm,N} = \frac{2kT}{\rho(\lambda_n\lambda_m)^{1/2}} \frac{\int \cdots \int_{C_N} y_n y_m \exp\left(-\sum_1^N y_i^2 \right) dy_1 dy_2 \cdots dy_N}{\int \cdots \int_{C_N} \exp\left(-\sum_1^N y_i^2 \right) dy_1 dy_2 \cdots dy_N}$$

and the condition now becomes:

$$\sum_{n=1}^N a_n y_n = C_N$$

where

$$a_n = X_n\left(\frac{2kT}{\rho\lambda_n}\right)^{1/2}.$$

We now rewrite each integral so that the integrations over y_n and y_m are the last ones; these integrations are carried from $-\infty$ to $+\infty$, and the condition is satisfied by keeping constant

$$\sum_{j=1}^N{}'' a_j y_j = C_{nm} = C_N - a_n y_n - a_m y_m$$

in the integration over the remaining $N-2$ variables, where the double accent signifies that j does not take on the values n and m.

The integration over this hyperplane, whose distance from the origin is $C_{nm}D_{nm}^{-1/2}$, where $D_{nm} = \sum'' a_j^2$, is carried out by rotating our coordinate system so that one of the axes coincides with the normal; the condition is now satisfied by keeping this variable constant and integrating over the others from $-\infty$ to $+\infty$. This transformation involves no calculation because the variables appear in the integrand in an invariant form, and we obtain:

$$L_{nm,N} = \frac{2kT}{\rho(\lambda_n\lambda_m)^{1/2}} \frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} y_n y_m \exp(-y_n^2 - y_m^2 - C_{nm}^2/D_{nm}) dy_n dy_m}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp(-y_n^2 - y_m^2 - C_{nm}^2/D_{nm}) dy_n dy_m}.$$

We now take the limit for $N \to \infty$ by appropriately changing the definitions of C_{nm} and D_{nm}. The remaining integrations are carried out in a straight-forward manner by transforming the expression in the exponent onto its principle axes, etc. We obtain:

$$L_{nm} = \frac{X_n X_m}{F^2(x)\lambda_n\lambda_m}\left[C^2 - \frac{kT}{\rho}F(x) \right].$$

In the above discussion we have assumed $n \neq m$; a similar calculation for L_{nn} shows that the general result may be written:

$$L_{nm} = \frac{X_n X_m}{F^2(x)\lambda_n\lambda_m}\left[C^2 - \frac{kT}{\rho}F(x)\right] + \delta_{nm}\frac{kT}{\rho\lambda_n}.$$

Note 4. We have to consider:

$$\frac{\partial G(L/2, t)}{\partial t} = \frac{2L}{a^2\pi^2}\sum_{n\text{odd}}\frac{1}{n^2}\cos\left(n^2a^2\pi^2/L^2 - \beta^2/4\right)^{1/2}t.$$

Let

$$H(t) = \sum_{n\text{odd}}\frac{1}{n^2}\cos\left(k_n^2 - w^2\right)^{1/2}t$$

where

$$k_n = \frac{na\pi}{L}, \quad w = \tfrac{1}{2}\beta$$

thus,

$$\frac{\partial G}{\partial t} = \frac{2L}{a^2\pi^2}H(t)$$

$$G(L/2, t) = \frac{2L}{a^2\pi^2}\int H(t)dt + A.$$

We now make use of a method due to Versluys.[8] He shows by making a Taylor expansion that:

$$\begin{aligned}\cos\left(k_n^2 - w^2\right)^{1/2}t &= \cos k_n t - \frac{w^2t^2}{1!}\frac{d}{d(t^2)}\frac{\cos k_n t}{k_n^2} + \frac{w^4t^4}{2!}\frac{d^2}{d(t^2)^2}\frac{\cos k_n t}{k_n^4} + \cdots \\ &= \left\{1 + \frac{w^2t^2}{1!}\frac{d}{d(t^2)}\int_C^t\int_0^t dtdt + \frac{w^4t^4}{2!}\frac{d^2}{d(t^2)}\int_C^t\int_0^t\int_C^t\int_0^t(dt)^4 + \cdots\right\}\cos k_n t \\ &= V\cdot\cos k_n t\end{aligned}$$

where:

$$c = \frac{L}{2a}$$

and the operation V through which $\cos k_n t$ is transformed into $\cos\left(k_n^2 - w^2\right)^{1/2}t$ is independent of k_n; it may be written as follows:

$$V = \sum_{p=0}^{\infty}\frac{(w^2t^2)^p}{p!}\frac{d^p}{d(t^2)^p}\int_C^t\int_0^t\cdots\int_C^t\int_0^t(dt)^{2p}.$$

Thus we have:

$$H(t) = \sum_{n\text{odd}}\frac{1}{n^2}V\cdot\cos\frac{n\pi at}{L} = V\cdot\sum_{n\text{odd}}\frac{1}{n^2}\cos\frac{n\pi at}{L}$$

as it can be proved (according to Versluys) that here the operations V and Σ can be interchanged. Now:

$$\sum\frac{1}{n^2}\cos\frac{n\pi at}{L} = \frac{\pi^2}{4}(\tfrac{1}{2} - at/L) \quad \text{for} \quad 0 \leqq t \leqq L/a$$

$$\therefore H(t) = \frac{\pi^2}{4}\cdot\left(\tfrac{1}{2}V\cdot 1 - \frac{a}{L}V\cdot t\right).$$

We find:

$$V\cdot 1 = \sum_{p=0}^{\infty}\frac{(w^2t^2)^p}{(2p)!} = \cosh wt = \cosh\tfrac{1}{2}\beta t$$

and

$$V\cdot t = t\sum_{p=0}^{\infty}\frac{(wt)^{2p}}{2^{2p}(p!)^2} = tI_0(wt) = tI_0(\tfrac{1}{2}\beta t).$$

[8] W. A. Versluys, Proc. Acad. Amst. **31,** 670 (1928).

Therefore

$$\frac{\partial G}{\partial t} = \frac{L}{4a^2}\left[\cosh \tfrac{1}{2}\beta t - \frac{2at}{L} I_0(\tfrac{1}{2}\beta t)\right]$$

$$G = \frac{L}{2a^2\beta}\left[\sinh \tfrac{1}{2}\beta t - \frac{2at}{L} I_1(\tfrac{1}{2}\beta t)\right];$$

here we have used the fact that

$$\int z I_0(z)dz = z I_1(z)$$

and evaluated A so as to make $G(L/2, 0) = 0$, which gives $A = 0$.

For other intervals than the one used above, the series

$$\sum \frac{1}{n^2} \cos (n\pi at/L)$$

represents a "saw tooth" function having discontinuities in its first derivative at the points nL/a, $n = 1, 3, 5 \cdots$ and the attempt to extend the calculation past the point $t = L/a$ was not successful.

TRANSITION PROBABILITIES AND QUENCHING IN THE 3P STATE OF SODIUM

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Abstract

The effect of foreign gases upon the fluorescence of sodium vapor excited by the second line of the principal series has been investigated. The gases used were helium, nitrogen, and hydrogen and the intensities of both the 3303A line and the D light were observed. From the variation in intensity of the 3303A line as gas is added it is concluded that the presence of an inert gas has no appreciable effect upon the relative transition probabilities in the 3^2P state of sodium. With nitrogen or hydrogen as the added gas the D light intensity variation followed that of the 3303A line very closely but with helium a marked increase in intensity was produced by the first gas added with a decrease at higher pressures. This increase was explained as due to a transfer of sodium atoms from the 3^2P to the 3^2D state by collisions, thus increasing the number of atoms which radiate the D light. In addition to this increase in number the collisional transfers produced an increased "Doppler width" in the D light which persisted up to pressures well over 100 mm of helium and caused a decreased absorption of the fluorescence light. The bearing of this work on the difference in the intensity ratio of the 2^2S-3^2P and 1^2S-3^2P transitions as reported by Weiss for an arc and by Christensen and Rollefson in fluorescence is discussed. It is concluded on the basis of experimental evidence that any explanation of the difference which depends upon multiplicity of the 3^2P state is incorrect. An explanation of this difference based upon the assumption that the life period of an excited atom varies inversely as the transition probability of the radiation emitted is presented. It is shown that recent work on the life periods of atoms in the 2^3S_1 state of mercury at least partially supports this assumption. A new type of sodium arc with increased intensity and stability of operation is described.

WHEN transitions by radiation are possible from one energy level to two or more lower energy levels, the relative numbers of each of these possible transitions is designated by what is known as the transition probability. This transition probability has generally been assumed to be a constant, independent of the method of excitation or of the environment of the radiating atom.

Recent investigations concerning the transitions from the $3P$ state of sodium by Weiss,[1] by Christensen and Rollefson[2] and by Prokofjew[3] have seemed to indicate that the transition probabilities in this case are dependent upon either the method of excitation or the environment of the radiating atoms.

Figure 1 shows the different possible transitions from the $3P$ state of sodium. For convenience in discussion they are labelled (a), (b) and (c). The

[1] Weiss, Ann. d. Physik **1,** 565 (1929).
[2] Christensen and Rollefson, Phys. Rev. **34,** 1157 (1929).
[3] W. K. Prokofjew, Zeits. f. Physik **58,** 255 (1929).

fine structure of the terms is not shown. The investigation by Weiss[1] concerning the radiation in a low-voltage arc shows the ratio of the probabilities of transitions (b) and (a) to be 25 to 1. The results of the investigation of Christensen and Rollefson[2] on the fluorescence of sodium vapor excited by the 3303A radiation from a sodium arc show this ratio to be 1.7 to 1. R. Ladenburg has made the suggestion that the method of correction for absorption used by Christensen and Rollefson may be in error due to the change in absorption coefficient with wave-length over the breadth of the line. With the formulas and tables presented in a paper by Ladenburg and Levy[4] the theoretical correction has been calculated. It is found that for the measurements taken with the center of the exciting cone at a depth of 3 mm approximately 80 percent of the *D* light should be absorbed while the absorption of the 3303A is too small to have any appreciable effect upon the calculation. If the data obtained by Christensen and Rollefson are recalculated and the theoretical correction for absorption introduced, a value of 5.7 is obtained.

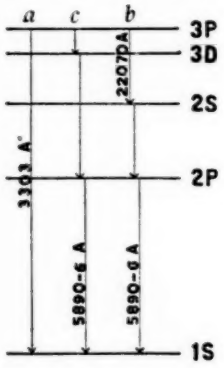

Fig. 1.

The calculation of this correction is, however, subject to serious errors due to the data upon which it was based. The experimental arrangement used by Christensen and Rollefson[2] was such that a fairly constant temperature could be maintained but no attempt was made to obtain an accurate measurement of the actual temperature of the fluorescence tube. A variation of approximately 15°C in the temperature produces a change of a factor of two in the vapor pressure of sodium. If the temperature used were fifteen degrees too high the correction for absorption would change to approximately 66 percent giving a ratio of 3.4. The data found for the vapor pressure of sodium itself do not agree within a factor of two.

That some error is involved is indicated by the fact that the ratios calculated from the data at two different depths differ by over twenty percent. The only experimental errors which might contribute to such a discrepancy are the photometric ones which do not exceed ten percent. If we assume that this discrepancy is due to an incorrect value for the vapor pressure of sodium and repeat the calculation for different pressures we find the same value for

[4] Ladenburg and Levy, Zeits. f. Physik **65**, 189 (1930).

both depths if we select the conditions so that the corrected ratio is 3.4. We feel that this represents the best value which can be obtained from the data.

The results of the calculations carried out by Prokofjew[3] based upon the methods of wave mechanics, give a value of 2.1 for the ratio of these two transition probabilities.

The value of this ratio calculated by Christensen and Rollefson on the basis of their measurements of the relative intensities of the 5890A and 3303A radiation in fluorescence depends upon the assumption that the probability of transition (c) is negligible with respect to (b), Fig. 1, since both of these transitions must eventually result in the radiation of 5890A. In order to test the validity of this assumption the calculations carried out by Prokofjew[3] were extended to give an estimate of the relative probabilities of transitions (b) and (c) and it is found that this ratio is large enough (of the order of 50 to 1) that radiation due to transition (c) may be neglected.

In this investigation the effect of the addition of foreign gases upon the fluorescence of sodium, excited by 3303A, is studied. In order to carry out the investigation quantitatively it was found necessary to design a new type of arc of greater intensity and stability of operation than any of those thus far described in the literature.

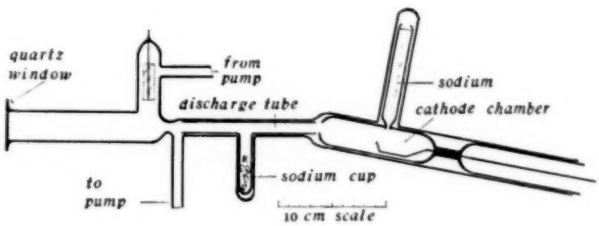

Fig. 2.

Figure 2, drawn to scale, gives the design of the arc. The quartz window and removable cathode are both sealed to the Pyrex with Dennison sealing wax. The electrical leads through the Pyrex are of tungsten and the anode is a cylinder of sheet nickel sealed to the tungsten wire with German silver. The cathode is of metallic sodium held in place by the cathode chamber, as shown in the diagram, with the electrical contact made directly to the tungsten wire.

The cathode chamber is made removable to facilitate refilling in case this becomes necessary. The sodium is introduced by placing a tube containing purified metal in the charging tube, as shown in the diagram, with one constricted end inserted in the small hole in the cathode chamber, sealing off the end of the charging tube, evacuating, and then heating the charging tube until the sodium melts and runs down. The discharge tube and sodium cup are placed inside a larger tube of the same shape to prevent the hot sodium from coming in contact with the wall which must remain vacuum tight. The sodium in the cup can be introduced in small tubes which are cut short enough to allow them to be inserted through the front of the arc before the quartz window is attached. The cup and discharge tube are equipped with heaters

and temperature controls, although the heat produced by the discharge is generally enough to maintain a sufficiently high temperature in the discharge tube. Argon is circulated through the arc as indicated, by means of a mercury pump with two liquid air traps filled with beads to remove the mercury vapor from the gas stream.

The sodium used is purified by first heating it for several hours, under vacuum, in such a way that it continually distills on to the sides of the flask and runs down again. This is done to expel occluded gases, especially hydrogen. When a very high vacuum is obtained the sodium is distilled through a side tube of large diameter and collected in tubes.

This arc is similar to that designed by Christensen and Rollefson[5] which we shall hereafter refer to as the "old type," but differs from it in several important respects. In the old type the cathode was heated and used as a part of the light source. In the new type it is not heated but is allowed to cool as much as possible and is not used as a part of the light source. The entire radiation, with appreciable intensity, is produced in the discharge tube in which the vapor pressure of sodium is controlled by the temperature of the sodium cup, the temperature of the discharge tube being always kept slightly higher. One advantage of this is the more accurate control of the vapor pressure of sodium which it affords, this being one of the chief factors involved in producing a discharge with constant intensity.

It is also found that the cool cathode eliminates a large degree of uncertainty of operation which was experienced with the old type. The trouble was undoubtedly connected with some sort of surface phenomenon, for it was always observed that whenever the "active point," usually visible on the surface of the cathode, was replaced by a diffused glow over the entire surface, the current dropped to a very small value with a corresponding decrease in intensity. This behavior was usually followed by complete failure. It was often found, however, that after allowing the cathode to cool, the arc could again be started at its normal current and also that heating the cathode to a higher temperature would result in breaking the discharge or reducing the current. It was further found that, whenever the $H\alpha$ line was present in the spectrum of the discharge, almost certain failure of the arc occurred. In view of this fact a tube of hot copper oxide was placed in the stream of circulating gas which reacted with the hydrogen changing it to water vapor which was removed in the same liquid air traps used to remove mercury vapor. This, of course, could remove only that portion of the hydrogen, present or produced in the back of the arc, which diffused into the circulating stream.

These difficulties are all eliminated in the new type of arc. The entire surface of the cathode chamber is usually found covered with sodium and the "active point" is seen to travel in a very devious path all over the surface. Even when the $H\alpha$ line is present in the spectrum of the discharge in appreciable amounts, this arc operates quite satisfactorily. In the old type whenever the cathode chamber was removed, after a few hours operation, it was always

[5] Christensen and Rollefson, Phys. Rev. **34**, 1154 (1929).

found to be cracked and had to be replaced. In the new type the cathode chamber does not crack and can be used again if refilling becomes necessary.

When the vapor pressure of sodium in the discharge tube is too low the arc will "flicker" but as the vapor pressure is increased the flickering ceases and a very steady discharge is maintained. As the vapor pressure is still further increased the intensity of the 3303A line gradually decreases. The optimum pressure is very easily obtained by increasing the temperature of the cup until the flickering just ceases.

The arc operates quite satisfactorily with about 0.5 cm of argon circulating through it. At lower pressures of argon the sodium diffuses out of the discharge tube quite rapidly, while increasing the pressure decreases the intensity of the 3303A line due to the quenching effect.

One of these arcs has been operated with 220 volts direct current at 2.5 amperes for about 150 hours and it seems in as good a condition as when new. This arc was operated with as low as 90 volts but some difficulty in starting it was encountered without the higher potential. A high frequency spark was used to start the arc.

This current of 2.5 amperes is by no means the maximum possible. By using less resistence in series with the arc the current can be increased to several times this value and one of these arcs was operated at 6 amperes for a period of one-half hour with perfectly satisfactory results.

For studying the fluorescence the apparatus assembly was identical with that described by Christensen and Rollefson with the addition of a small-diameter quartz tube, with a graded seal to Pyrex, leading from the fluorescence tube to the apparatus used to introduce varying pressures of foreign gases. The mean free path of sodium atoms in the pure vapor is so large, at the temperatures used, that the leak of sodium vapor through this tube is negligible. The foreign gas was always introduced while the fluorescence tube was cold, in order to prevent sodium vapor from being swept to the front and condensed on the window. It was found that addition of the foreign gases increased the necessary temperature of the hot air stream used to prevent condensation of sodium on the windows. An air stream of about 400°C was used with the fluorescence tube at 180–200°C. It was also found that with the air stream at this temperature, the temperature of the fluorescence tube necessary to cause "browning" was very much greater than when the air stream was kept at 280°C. This indicates that "browning" is preceded by condensation of sodium.

The assembly was constantly checked for stray light by making exposures for long periods with the fluorescence tube cold.

The helium gas used was passed through charcoal at both liquid air and liquid hydrogen temperatures. The nitrogen was passed through a tower filled with copper turnings and ammonium hydroxide to remove oxygen and then through a liquid air trap. The hydrogen was made electrolytically and was passed over hot copper to remove oxygen and then through charcoal at liquid air temperature.

The Wratten and Wainright panchromatic plate was used and a standard

developer and development procedure was adopted in order that blackenings on different plates might be compared. All the plates used were from the same box. All the photographs used to plot any one curve were taken on the same plate. The exposures of the fluorescence excited by 3303A radiation were taken over periods of one-half hour, one hour, two hours and three hours. The longer exposures were used in order to get blackenings of a density most accurately determinable, when the intensity was diminished by the addition of foreign gases. Photographs were also taken of the fluorescence when excited by *D* light. When a screen of approximately 10 percent transmission was inserted in the exciting beam, exposures of 10 seconds, 20 seconds, 40 seconds and 80 seconds gave satisfactory blackenings.

The photographic blackening densities were determined with a Zeiss microphotometer. All the photographs of the fluorescence and those taken to obtain the blackening—intensity calibration curves were photometered with the same adjustments of the instrument, and the readings were recorded on the same arbitrary scale. The blackening of any photograph could then be translated into intensity in terms of percent of an arbitrary standard.

The calibration curves were obtained with a direct current helium discharge operated by a 600 volt battery assembly at a current of 0.36 milliamperes in the case of the longer exposures and 0.8 milliamperes for the shorter exposures. The current was easily controlled to within 2 percent by gradually decreasing the resistance in series as the operating voltage of the battery decreased.

This discharge has strong lines at 5875A and 3187A as compared to 5890A and 3303A in the sodium fluorescence. A consideration of Harrison's work in spectral photometry, indicates that the use of these lines for calibration purposes is justified within a limit of 2 percent accuracy. For the longer-exposure calibrations a filter of $CrCl_3$ solution in a quartz vessel was placed between the discharge and the spectrograph. This absorbs a certain percentage of the 5875A radiation which is the more intense of the two and by varying the concentration of the solution the blackening produced by the two lines can be made approximately equal. This makes it possible to determine the calibration curves for both wave-lengths at the same time. For the calibration curves used with *D*-light excitation the $CrCl_3$ filter was not inserted since only the intensity of the 5875A line was needed.

Screens, calibrated for transmission with a thermopile, were used to reduce the intensity by a known fraction. The screens were kept moving and when two screens were used simultaneously they were moved in opposite directions at all times.

Photographs were obtained of the fluorescence excited by 3303A radiation and by *D* light with varying pressures of helium, nitrogen and hydrogen in the fluorescence tube and the resulting intensity curves are given below.

In Fig. 3, which shows the effect of helium on the fluorescence, curve *A* gives the variation in intensity of the 3303A line, the dots represent intensities with the fluorescent cone at a depth of 3 mm from the observer's side of the fluorescence vessel and the crosses are for a depth of 10 mm, the circles re-

present a theoretical quenching curve. Curve *B* gives the intensity of the "*D*" light when excited by 3303A the fluorescent cone being at a depth of 3 mm, curve *C* gives the intensity of "*D*" light with the cone at a depth of 10 mm. Curve *D* gives the intensity of *D* light excited by *D* light. In each case the intensities are in terms of the intensity with no helium present.

From the energy-level diagram for sodium, Fig. 1, it may be seen that the decrease in intensity of the 3303A line may be explained in two different ways. It may be due to transfers, by collisions of the second kind, of atoms in the $3P$ state to any one of the other four states designated. In other words it may be

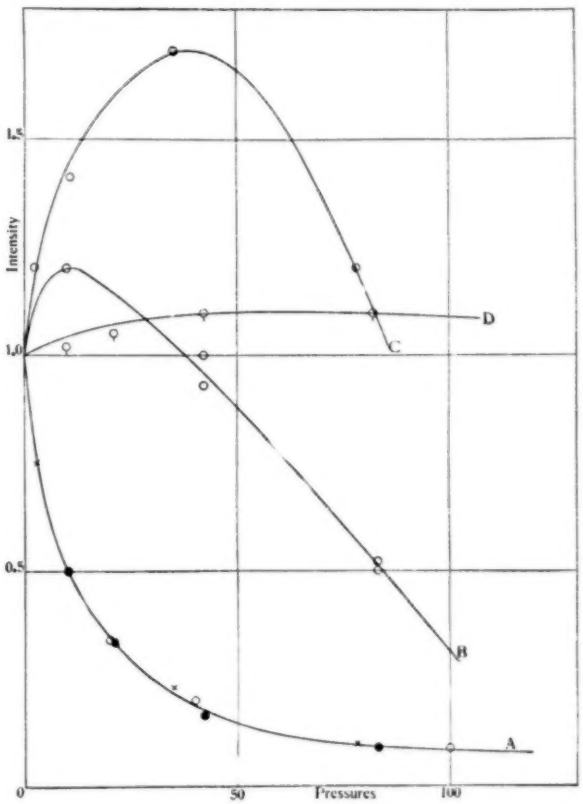

Fig. 3.

purely a quenching phenomenon. Also, it may be due to a change in the relative transition probabilities, effected by the presence of the helium, in favor of transitions "*b*" or "*c*". A combination of these two effects is also possible.

If the collisional transfers occur to either the $3D$, $2S$ or $2P$ state the effect upon the relative intensities of the 3303A and 5890A radiation is exactly the same as that produced by a change in the relative transition probabilities. However, the dependence of each of these effects upon the pressure of foreign gas may serve as a method of distinguishing them.

A theoretical quenching curve is determined by the expression for the fractional decrease in intensity

$$100 - I = \tau/(\tau + T),$$

where τ is the mean life of the excited atom, T is the mean time between effective collisions and I is the percent of the intensity of the unquenched radiation. At the pressure designated by $p_{1/2}$ at which the intensity has been reduced 50 percent it is evident that τ is equal to T, and we then have the following relations

$$T = k/p; \quad \tau = k/p_{1/2}$$

where p is the pressure at constant temperature and k is a proportionality factor. We may then write

$$100 - I = \frac{k/p_{1/2}}{k/p_{1/2} + k/p} = \frac{1}{1 + p_{1/2}/p}. \tag{1}$$

Replacing $p_{1/2}$ in Eq. (1) by the value obtained from any quenching curve gives the theoretical formula for that curve.

The small circles near curve A, Fig. 3, represent points on a theoretical quenching curve with the value for $p_{1/2}$ taken from curve A. The excellent agreement between the observed and calculated curves is evidence in favor of the supposition that the decrease in intensity of the 3303A radiation is due to a collisional effect and that the presence of helium has no apparent effect upon the relative transition probabilities.

Any effect upon the transition probability which depends upon the interaction of the excited sodium atom and a foreign gas molecule, at the instant of radiation, such as the effect of the electrostatic field, would be directly proportional to the pressure and independent of the life period of the excited atom since only its position at the instant of radiation is of importance. This straight-line relation might be slightly altered by the second order effect of multiple interaction. If the time required for the act of radiation is finite and if at any time during the act, interaction with a foreign gas molecule is effective in changing the transition probability the change in intensity will take the form of a quenching curve, but the value of τ will be different from that in the true quenching formula and the two effects cannot be superimposed. The two phenomena are indistinguishable only in case the effect of the foreign gas molecule is such that at any time during the normal life period of the excited atom, that interaction occurs, it may be caused to radiate or be so affected that when it does radiate its relative transition probabilities will have been changed. In case successive collisions are effective in changing the transition probability, the intensity variation will depend upon some higher power of the pressure.

Curve D, Fig. 3, gives the observed intensity for D light when excited by D light, and when compared with the data obtained by Mannkopff[6] using a resonance lamp for excitation it is evident that a considerable amount of increased absorption has occurred due to the pressure broadening of the absorption line. This is to be expected since the center of the incident D line is

[6] Mannkopff, Zeits.f. Physik **36**, 315 (1926).

very markedly absorbed and at the point of observation the excitation is due mainly to the remaining broadened portion. Consequently, the intensity is greatly affected by any broadening of the absorption line. In the case of the 3303A excitation, since the amount of absorption is very small there is still sufficient intensity in the center of the incident line at the point of observation to render the broadening effect negligible. This is verified by the close agreement between curve *A* and its theoretical quenching curve.

Curves *B* and *C*, Fig. 3, which give the intensity variation of *D* light when excited by 3303A, show the resultant of two effects—the increase in intensity due to collisional transfer of atoms from the $3P$ to the $3D$, $2S$ or $2P$ states, and the decrease in intensity due to complete quenching of atoms in any one of these states.

Boeckner[7] found that the probability of caesium atoms in the $4P$ state being transferred by collision to the $5D$ state was approximately twenty times that of being transferred to the $3S$ state. The energy difference in the first case is 0.043 volts and in the second case 0.18 volts, a factor of approximately 4. By analogy it seems certain that most of the collisional transfers from the $3P$ state of sodium will be to the $3D$ rather than to the $2S$ state, since the ratio of the energies involved is almost identical with that in the caesium atom, as are also the important quantum numbers. It may certainly be assumed that the number of atoms transferred to the $1S$ state, an energy difference of approximately 30 times as great as that between the $3P$ and $3D$ states, will be negligible. The increase in intensity due to the collisional transfers is not solely a matter of increasing the number of atoms radiating *D* light but also involves a decrease in the absorption because of an increased "Doppler width" of the fluorescence light. If it were not for the latter effect curves *B* and *C* should be identical, however, with this change in absorption the observed rise in intensity of the *D* light will be greater for the greater depths. The two curves will coincide when enough collisions occur between the time the atom is changed from the 3^2P state by a collision and the time at which the quantum of "*D*" light is emitted to restore the atoms to the normal distribution of velocities. From the results we have obtained it is obvious that this does not occur except at pressures well in excess of 100 mm of helium which means that the fast moving excited sodium atoms retain their high speeds for a large number of collisions. The fact that at high pressures the "*D*" light intensity drops below that which would be calculated from Mannkopff's data on quenching indicates that under these conditions some quenching to the 1^2S state occurs.

Figure 4 gives the results obtained when nitrogen and hydrogen were introduced into the fluorescence tube. In each case only the data for the 3303A line are plotted as the curves for the "*D*" light did not differ from these to any marked degree. The absence of any increase in the "*D*" light intensity such as was found with helium is taken to indicate that for these gases the quenching process involves returning the sodium atom to the 1^2S state. On the nitrogen

[7] Boeckner, Bur. Standards J. Res. 5, 13 (1930).

curve the dots represent the experimental points and the circles give the theoretical form for the quenching curve. From the close agreement between the two sets of points we may conclude that nitrogen has no pronounced effect upon the transition probabilities in the 3^2P state of sodium.

The data for the hydrogen curve are subject to some uncertainty due to the fact that the presence of hydrogen seems to accelerate the reaction between sodium and quartz causing a change in the transmission of 3303A through the windows. However, the observed points follow a theoretical quenching curve so well that it may be said that hydrogen has no effect on the transition probabilities.

The most probable source of error in the measurements is in the variation in the intensity of the arc and in the temperature controls throughout the

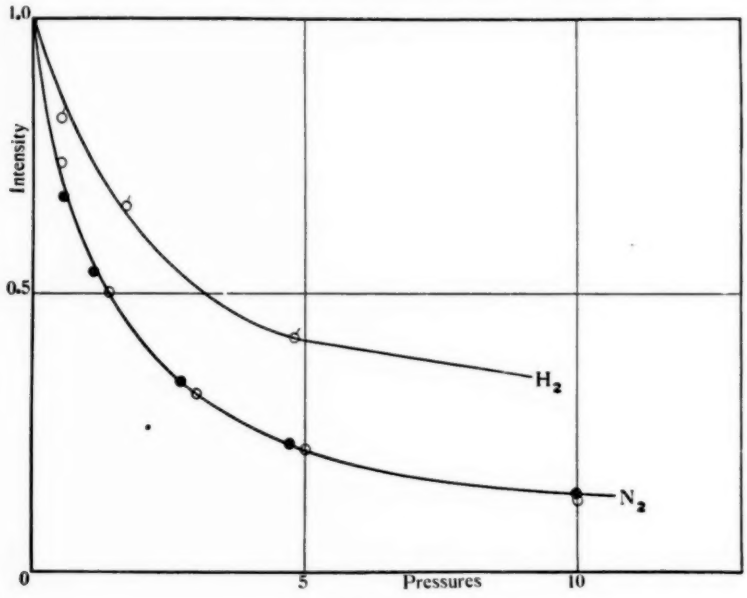

Fig. 4.

apparatus. This was checked by taking a series of consecutive photographs of the fluorescence, as used in the experiments. These were taken over a period of 4 hours and a deviation of not greater than 10 percent in the intensity was observed. The accuracy of the photometry was well within this limit. It seems, therefore, that an error of not greater than 10 percent is to be expected in the measurements.

The results of this investigation demonstrate that there is no apparent effect upon the transition probabilities in the $3P$ state of sodium when the excited atoms are subjected to the presence of an inert gas. Therefore, some other phenomenon must be responsible for the difference between the intensity ratio obtained by Weiss and that obtained by Christensen and Rollefson.

A separation of the $3P$ level into two or more levels having different transition probabilities and different populations might be assumed as a possible

explanation. This separation may or may not be the nuclear hyperfine structure. Let it be supposed that in the pure fluorescence the number of collisions during the mean life capable of transferring excited atoms from one of these states to the other is negligibly small. The radiation observed might be supposed to come largely from a state in which the ratio of the probabilities of transitions (b):(a) is small, with a smaller amount coming from a state in which this ratio is much higher. The high pressure of inert gas present in the arc as used by Weiss, due to transfers by collisions of the second kind, would tend to make the population in both states equal. It is then evident that the ratio of the intensities of these two transitions would be immediately increased.

This same effect, however, should be observed when inert gas is introduced into a fluorescence tube. It should appear in the investigation presented here as a decrease in the intensity of the 3303A radiation on the addition of helium. An obvious assumption would be that at least every kinetic theory collision would be effective in transferring atoms between states differing by so small an amount of energy as must be assumed between such states as those being considered here. At 10 mm pressure of helium, sodium atoms in the $2P$ state undergo on the average 4.5 kinetic theory collisions during the mean life of the excited atom. The figure for the $3P$ state should be at least as great. It is therefore to be expected that equilibrium between states within the $3P$ state should be reached at this pressure. A change in the ratio of the probabilities of transitions (b) and (a) from 1.7:1 to a ratio of 25:1 would result in a 90 percent decrease in the intensity of the 3303A radiation. From curve *A*, Fig. 3, it may be seen that at 10 mm pressure the intensity of the 3303A radiation has been decreased only 50 percent. This seems to be conclusive evidence that the explanation presented above is not valid.

The difference in the method of excitation has been suggested as a possible explanation, but if this difference is postulated as a method of putting atoms into different states within the $3P$ state, the argument is subject to the same objection presented in the preceding paragraph. In the arc there should be complete equilibrium and in the fluorescence equilibrium should be quickly established on the addition of inert gas, but this is found to be not the case. If it is assumed that the method of excitation causes some permanent change in the $3P$ state as an entity, the above objection no longer holds.

In general it may be said with some degree of certainty that the experimental evidence obtained in this investigation presents a very serious objection to any explanation of this disagreement in intensity ratios which depends upon a difference in transition probabilities of states within the $3P$ state.

Another possible explanation suggests itself when one makes an assumption concerning the actual mechanism of radiation of which so little is known. It seems not impossible to imagine that this mechanism is such that when more than one transition is possible, on the average that transition of greatest probability will occur in the shortest length of time; or, in other words, that the life period of the excited atom varies inversely as the transition probability of the radiation which occurs. This may be stated in another way: that

the chance of that radiation occurring which has the least probability increases with increasing life of the excited atom. It is doubtful that there is as yet any experimental evidence which can conclusively prove or disprove this assumption.

If this assumption is made, however, the explanation sought is immediately forthcoming. The measurements of Weiss were made by observing the radiation from sodium atoms in the $3P$ state in the presence of argon at a comparatively high pressure. It is then to be expected that something over 90 percent of the atoms in the $3P$ state were transferred to the $3D$ state before they could radiate and the relative intensities measured were of the radiations emitted by only those atoms which had survived this collision process. The number of collisions increases with increasing life period, consequently more of the atoms with shorter life periods than of those with longer life periods will survive the collision process. The relative intensities of the radiations will then change in favor of that one having the shorter life period; or on the basis of the assumption suggested above, the relative intensities would change in favor of the transition with greatest probability. In the case of the $3P$ state of sodium it would then be expected that the ratio of the intensities of the transitions (b):(a), Fig. 1 would be greater in the presence of a high pressure of argon than in the pure fluorescence, since transition (b) is the one of greatest probability.

The assumption suggested above is at least partially vindicated by the work of Randall[8] and of Richter[9] who found independently and by entirely different methods that the life periods of the atoms in the 2^3S_1 state of mercury appear approximately four times as great when the 5461A radiation is observed as when either the 4358 or 4047 line is observed. As an explanation of this it was suggested that the life periods and transition probabilities might be different for each hyperfine structure level, and Frisch and Pringsheim[10] attempted to demonstrate this by exciting mercury atoms to the 2^3S_1 state by different methods but found no variation in the relative intensity.

Mrozowski[11] gives some theoretical evidence against the possibility of any influence of nuclear moments on the life period but suggests that there is some sort of separation of the 2^3S_1 state into states with different life periods and different transition probabilities.

In the investigation carried out by Randall no complexity was observed in the constant k which was used in the formula C^{-kt} to describe the falling off of intensity with time after excitation. This indicates that all of the atoms radiating a particular wave-length had the same life period, and therefore probably existed in the same state. This prerequisite would be complied with if all the radiation was assumed to come from the same level but from atoms whose life periods depended upon the wave-length radiated.

Another very serious objection to any explanation of this difference in life

[8] Randall, Phys. Rev. **35,** 1161 (1930).
[9] Richter, Ann. d. Physik **7,** 293 (1930).
[10] Frisch and Pringsheim, Zeits. f. Physik **67,** 169 (1930).
[11] Mrozowski, Zeits. f. Physik **68,** 278 (1931).

periods which depends upon a multiplicity of the 2^3S_1 state is encountered when we consider the experiments which have been performed demonstrating the extremely large efficiencies or collisional radii for processes involving such small energy differences as there must be between such states.[12] It seems almost necessary to assume that in the experiments performed by Randall complete equilibrium between the populations of such states must necessarily have been established, and if this were the case a difference in life periods could not have been measured. It is also impossible that there could have been only a partial equilibrium since Randall found that varying the pressure had no effect upon the life periods measured. It seems therefore almost necessary to assume that either the life periods of atoms in any excited state may depend upon the wave-length radiated or else that there are states within the one state with different life periods and transition probabilities between which strong argument in favor of the explanation based upon a change in relative intensity due to quenching, which is presented above concerning the disagreement in the intensity ratios in the $3P$ state of sodium.

[12] Experiments by Wood and Mohler, Phys. Rev. **11,** 70 (1918), have shown that when Na vapor is excited by a single D line and the temperature of the fluorescence is above 220°C, both D_1 and D_2 appear in the fluorescence due to transfers by collision from one member of the doublet P state to the other. Datta, Zeits. f. Physik **37,** 625 (1926), in experiments on the depolarization in the resonance fluorescence of sodium finds an effective radius of approximately 10^{-4} cm, or approximately ten thousand times that of the normal kinetic theory radius.

A NOTE ON LOCAL MOMENTUM IN WAVE MECHANICS

By Lloyd A. Young*
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Abstract

The present paper shows the exact relations between dynamical quantities of classical theory and their wave mechanical analogues. A new quantity *local momentum* is defined and discussed and the Bohr quantum condition is revived in a form compatible with modern theory.

1. THE one-dimensional Schrödinger equation for a particle moving in a force-free field is

$$\psi'' + p^2\psi = 0 \tag{1}$$

where p and p^2 are quantities proportional to the momentum and energy of the particle respectively.[1] This equation possesses the particular solutions

$$\begin{aligned} \psi^+ &= A^+ e^{+ipx} \\ \psi^- &= A^- e^{-ipx} \end{aligned} \tag{2}$$

representing the streaming of particles in the positive and negative directions of x. The constants A^+ and A^- are arbitrary and are used to normalize the intensity of the stream of particles to any desired quantity. The corresponding wave equation for a general scalar potential field $V(x)$ is

$$\psi'' + [E - V(x)]\psi = 0. \tag{3}$$

We may assume particular solutions of this equation of the form[2]

$$\psi^\pm = A^\pm(x) e^{\pm i\int P dx} \tag{4}$$

and adopt the terminology *local amplitude* for $A^\pm(x)$ and *local momentum* for $P(x)$. Both $A^\pm(x)$ and $P(x)$ may be taken as real quantities (since any complex number may be written in the form $ae^{i\theta}$ with a and θ real). Substitution of (4) into (3) leads, upon separately equating real and imaginary terms to zero, to the following differential equations for $A^\pm(x)$ and $P(x)$.

$$A^{\pm\prime\prime} - A^\pm P^2 + [E - V(x)]A^\pm = 0 \tag{5a}$$

$$2A^{\pm\prime}P + P'A^\pm = 0. \tag{5b}$$

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[1] Throughout this note units are chosen in such a manner that all equations may be written in their simplest form. It is extremely easy to rewrite all results in the usual system of units.

[2] This substitution is well known in mathematics but its use in wave mechanics has been extremely limited.

The second of these gives an immediate relation between $A^{\pm}$ and P; namely

$$A^{\pm} = P^{-1/2} \tag{6}$$

Eq. (5a) may then be written in terms of $P(x)$ alone

$$P^2 + V - P^{1/2}\frac{d^2}{dx^2}P^{-1/2} = E \tag{7}$$

or if we define the quantity *local kinetic energy* by the relation $T^* = P^2$ we have

$$T^* + V - T^{*1/4}\frac{d^2}{dx^2}T^{*-1/4} = E. \tag{7a}$$

This equation is exact and is the wave mechanical analogue of the classical conservation of energy law.

Now we have as particular solutions of the wave equation corresponding to pure travelling waves in the case of free motion[3]

$$\begin{aligned} \psi^+ &= a^+P^{-1/2}e^{i\int Pdx} \\ \psi^- &= a^-P^{-1/2}e^{-i\int Pdx}. \end{aligned} \tag{8}$$

For the corresponding probability densities we have

$$\begin{aligned} \bar{\psi}^+\psi^+ &= \overline{a^+}a^+/P \\ \bar{\psi}^-\psi^- &= \overline{a^-}a^-/P. \end{aligned} \tag{9}$$

The most general real solution of (3) representing the wave solution for a discrete state of the system may be written

$$\psi = aP^{-1/2}\cos\left[\int_{x0}^{x} Pdx + \text{phase factor}\right]. \tag{10}$$

If the range of x is, for example, from $-\infty$ to ∞ we may show that in order that ψ satisfy the usual boundary conditions we must have

$$\int_{-\infty}^{\infty} Pdx = n\pi \tag{11}$$

where n is a positive integer. Since ψ_n is the n-th characteristic solution of a Sturm-Liouville differential equation it must possess n-1 roots in the finite region of x. This is just the number of roots possessed by $\cos \int Pdx$. It is easy to show that $P(x)$ does not vanish for finite x by a simple study of Eq. (7).

2. The comparison of the preceding equations with classical equations is extremely interesting. Eq. (7a) is to be compared with the classical equation

$$T + V = E$$

in which T is the ordinary kinetic energy. The probability densities (9) become identical with the classical expressions when the *local momentum* is re-

[3] With A and P depending on x either of the Eqs. (8) is capable of describing combinations of progressive and standing waves. As an example write $ae^{ipx}+be^{-ipx}$ in the form $A(x)e^{i\int Pdx}$.

placed by the ordinary momentum. $\int Pdx$ is the wave mechanical action integral and Eq. (11) is the analogue of the most fruitful equation of modern physics—the Bohr-Sommerfeld quantum condition

$$\oint pdx = nh.$$

The local momentum P becomes in the limit (in the sense of the correspondence principle) equal to the classical momentum.

3. As an example the *local momentum* for the two lowest states of the harmonic oscillator is plotted (Fig. 1) as a function of x along with curves of the classical momentum $p(x)$. The scale of x has been so chosen that the $p(x)$ curves which are usually pictured as ellipses are here shown as circles. For all

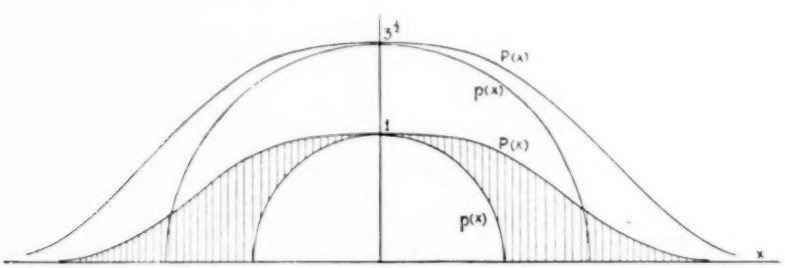

Fig. 1. Comparison of local and classical momentum for the first two states of the harmonic oscillator.

states the area corresponding to the shaded area for the lowest state is $\pi/2$. This alone will show that $P(x)$ and $p(x)$ must approach one another for high quantum states.

4. The present note is not intended to be complete and further investigations are in progress 1*st* on the fundamental nature of P and 2*nd* the application of the results of this paper to various quantum theory problems. In conclusion the writer wishes to express his appreciation to Professor G. E. Uhlenbeck who aroused his interest in the problem of the relation between quantum and classical physics and to Professors J. C. Slater, P. M. Morse and N. H. Frank, of the Massachusetts Institute of Technology, and to M. H. Johnson, Jr., of Harvard University, for their comments and criticism of the manuscript of this note.

Author's Note Added in Proof: Attention should be called to two articles which are related to this note namely H. A. Wilson, Phys. Rev. **35,** p. 948 and W. E. Milne, Phys. Rev. **35,** p. 863. Neither of these writers, it is apparent, realized the rich physical content of their equations.

VALENCE FORCES IN LITHIUM AND BERYLLIUM

By J. H. Bartlett, Jr. and W. H. Furry
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(Received September 2, 1931)

Abstract

With the nodeless wave functions of Guillemin and Zener, the method of Heitler and London is applied to determine how two normal lithium atoms, and also two normal beryllium atoms, influence each other (as a function of the distance). For the diatomic lithium molecule in the ground state, the equilibrium distance is calculated to be 2.4A, and the heat of dissociation to be 1.09 volts. The experimental values are 2.67A (Harvey and Jenkins) and 1.14 volts (Loomis and Nusbaum), respectively. Two normal beryllium atoms repel each other.

AN ACCURATE determination of the heat of dissociation and of the equilibrium separation of the nuclei in a diatomic molecule demands, if one uses the method of Heitler and London,[1] that the eigenfunctions of the individual atoms be known to a high degree of precision. Guillemin and Zener,[2] and later Zener[3] have succeeded in finding eigenfunctions for the atoms in the second row of the periodic table (starting with lithium), which are simple in form and give a quite accurate value for the ionization potential. This indicates that the valence electron is represented quite well, and that one should expect these eigenfunctions to be suitable for use in calculating the molecular constants.

In the present paper, we have made use of such functions. The first part is devoted to a revision of a calculation made by Delbrück,[4] who used atomic functions which gave a value of 3.9 volts for the ionization potential of lithium, as against the experimental value of 5.37 volts. In the second part, we investigate the interaction of two beryllium atoms, each in the normal state at infinite separation.

I. Molecular Constants of Li_2

Since Delbrück[4] has shown that the K-shells make only a very small contribution, we shall neglect them entirely. Accordingly, the lithium problem reduces to one which is analogous to that treated by Heitler and London,[1] the only difference being in the form of the atomic wave functions. We shall calculate (a) strictly along the lines of Heitler and London, using "nonpolar" wave functions, i.e., those which allow only one electron on each atom at infinite separation, and (b) according to the modification made by Slater,[5] which admits wave functions with two electrons on one atom and none on the other (corresponding to Li^- and Li^+, respectively).

[1] W. Heitler u. F. London, Zeits. f. Physik **44,** 455 (1927).
[2] V. Guillemin u. C. Zener, Zeits. f. Physik **61,** 199 (1930).
[3] C. Zener, Phys. Rev. **36,** 51 (1930).
[4] M. Delbrück, Ann. d. Physik **5,** 36 (1930).
[5] J. C. Slater, Phys. Rev. **35,** 509 (1930).

Unless otherwise stated, the notation used throughout this paper will be the same as that used by one of the writers previously.[6] For s electrons, a (1) will denote the wave function describing electron 1 on nucleus a.

We shall use the nodeless functions, namely

$$a(1) = ca_1e^{-\kappa a_1/2}, \text{ etc.}$$

(a) Calculation with nonpolar wave functions only

The zeroth approximation functions are:

$$^1\Sigma(S^N):\psi = a(1)b(2) + a(2)b(1)$$
$$^3\Sigma(A^N):\psi = a(1)b(2) - a(2)b(1).$$

The energies are:

$$^1\Sigma(S^N):E = \frac{J+K}{1+S}$$
$$^3\Sigma(A^N):E = \frac{J-K}{1-S}$$

where

$$J = \int H'[a(1)]^2[b(2)]^2 dv_1 dv_2$$
$$K = \int H'a(1)b(1)a(2)b(2)dv_1dv_2$$
$$S^{1/2} = \int a(1)b(1)dv_1$$
$$H' = \frac{2}{R} + \frac{2}{r} - \frac{2}{a_2} - \frac{2}{b_1}.$$

These energies are relative to the energy at infinite separation.

Writing

$$j = \int \frac{2}{r}[a(1)]^2[b(2)]^2 dv$$
$$k = \int \frac{2}{r}a(1)b(1)a(2)b(2)dv$$
$$I = \int \frac{2}{b_1}[a(1)]^2 dv_1$$
$$I' = \int \frac{2}{b_1}a(1)b(1)dv_1$$

[6] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).

we have

$$J = \frac{2}{R} - 2I + j$$

$$K = \frac{2}{R}S - 2S^{1/2}I' + k.$$

For the normalization, $2\pi c^2/\kappa^5 = 1/48$. From the previous paper,[6]

$$j = (4/9)(i_1 + i_3) + i_9/9.$$

Making the transformation

$$a = (R/2)(\lambda + \mu), \quad b = (R/2)(\lambda - \mu),$$

and using Neumann's expansion,

$$k = \int \frac{2}{r} c^4 a_1 a_2 b_1 b_2 e^{-(\kappa/2)(a_1+b_1+a_2+b_2)} dv_1 dv_2$$

$$= \frac{4}{R} \cdot 2\pi \int \sum_{\tau=0}^{\infty} D_{\tau 0} P_\tau \begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} Q_\tau \begin{pmatrix} \lambda_2 \\ \lambda_1 \end{pmatrix} P_\tau(\mu_1) P_\tau(\mu_2) \cdot c^4 (R/2)^{10} (\lambda_1^2 - \mu_1^2)^2 (\lambda_2^2 - \mu_2^2)^2 \cdot e^{-\alpha(\lambda_1+\lambda_2)/2} d\lambda_1 d\lambda_2 d\mu_1 d\mu_2.$$

The possible values of τ are 0, 2, and 4.

$$k^{(0)} = (\alpha/2)^9 (\kappa/288) \int Q_0 \begin{pmatrix} \lambda_2 \\ \lambda_1 \end{pmatrix} (\lambda_1^4 - 2\lambda_1^2/3 + \tfrac{1}{5})(\lambda_2^4 - 2\lambda_2^2/3 + \tfrac{1}{5}) e^{-\alpha(\lambda_1+\lambda_2)/2} d\lambda_1 d\lambda_2$$

$$= (\alpha/2)^9 (\kappa/144) \{ s_0(44) - (\tfrac{2}{3})[s_0(24) + s_0(42)] + (\tfrac{1}{5})[s_0(04) + s_0(40)] - (2/15)[s_0(02) + s_0(20)] + (4/9) s_0(22) + (1/25) s_0(00) \}$$

where[6]

$$s_\tau(m, n) = \int_1^\infty Q_\tau(\lambda_1) e^{-\alpha\lambda_1/2} \lambda_1^m d\lambda_1 \cdot \int_1^{\lambda_1} e^{-\alpha\lambda_2/2} \lambda_2^n d\lambda_2$$

and

$$\alpha = \kappa R.$$

Now let

$$v_\tau(m, n) = \int_1^\infty d\lambda_1 \int_1^\infty d\lambda_2 Q_\tau \begin{pmatrix} \lambda_2 \\ \lambda_1 \end{pmatrix} P_\tau \begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} \lambda_1^m \lambda_2^n e^{-\alpha(\lambda_1+\lambda_2)/2}.$$

In particular,

$$v_2(m, n) = (3/2)[s_2(m, n+2) + s_2(n, m+2)] - (\tfrac{1}{2})[s_2(m, n) + s_2(n, m)].$$

Then

$$k^{(2)} = (\alpha/2)^9 (\kappa/90) \{ (1/9) v_2(22) - (2/21) v_2(20) + (1/49) v_2(00) \}.$$

For $\alpha=5$, one finds $k^{(0)}=0.1876\kappa$ and $k^{(2)}=0.0012\kappa$, so that the latter contribution is almost negligible.

We shall omit the further details of the calculation, which is quite easy, and give the results.

TABLE I. *Integrals and energies.*

α	$\alpha=3$	4	5	6	7	8	9	10
s	0.7916	0.6642	0.5316	0.4061	0.2968	0.2081	0.1405	0.0914
I/κ	.4468	.4022	.3564	.3138	.2772	.2463	.2206	.1995
I'/κ	.4324	.3835	.3289	.2738	.2221	.1761	.1368	.1045
j/κ	.3367	.3177	.2969	.2746	.2527	.2316	.2121	.1948
k/κ	.2856	.2379	.1888	.1432	.1022	.0714	.0477	.0302
$^1\Sigma/\kappa$	.0858	−.0251	−.0614	−.0641	−.0548	−.0400	−.0267	−.0173
$^3\Sigma/\kappa$	.316	.203	.133	.0854	.0555	.0332	.0194	.0116

With a value[2] of $\kappa=1.26$, the equilibrium distance is found to be 2.4A and the heat of dissociation is 1.09 volts. This is to be compared with the experimental values of 2.67A and 1.14 volts, respectively.[7,8] Delbrück obtained values of 4.6A and 1.4 volts, which indicates that the atomic wave functions did not describe the behavior of the valence electron over a sufficient range. This is traceable to the fact that he used a wave function with a large radial node, while we have used a nodeless function.

(b) Calculation with polar wave functions included

When we allow the possibility of two electrons being on one atom, then we have four possible resulting states. The wave functions are

$$^1\Sigma,\ S^N \quad \psi_1 = \begin{vmatrix} a_\alpha(1)+b_\alpha(1) & a_\beta(1)+b_\beta(1) \\ a_\alpha(2)+b_\alpha(2) & a_\beta(2)+b_\beta(2) \end{vmatrix}$$

$$A^N \quad \psi_4 = \begin{vmatrix} a_\alpha(1)+b_\alpha(1) & a_\beta(1)-b_\beta(1) \\ a_\alpha(2)+b_\alpha(2) & a_\beta(2)-b_\beta(2) \end{vmatrix}$$

$$A^N \quad \psi_3 = \begin{vmatrix} a_\alpha(1)-b_\alpha(1) & a_\beta(1)+b_\beta(1) \\ a_\alpha(2)-b_\alpha(2) & a_\beta(2)+b_\beta(2) \end{vmatrix}$$

$$^1\Sigma,\ S^N \quad \psi_2 = \begin{vmatrix} a_\alpha(1)-b_\alpha(1) & a_\beta(1)-b_\beta(1) \\ a_\alpha(2)-b_\alpha(2) & a_\beta(2)-b_\beta(2) \end{vmatrix}$$

where α and β specify the two possible spin orientations.

The function ψ_1 will give an approximation to the normal state, but the state represented by ψ_2 can exert a perturbing effect, so that the correct zeroth approximation to the wave function of the normal state is a certain linear combination of ψ_1 and ψ_2.

The secular equation is

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{22}-E \end{vmatrix} = 0$$

[7] A. Harvey and F. A. Jenkins, Phys. Rev. **35**, 789 (1930).
[8] F. W. Loomis and R. E. Nusbaum, Phys. Rev. **37**, 1712 (1931).

where

$$H_{11} = \frac{\int \psi_1^* H \psi_1 dv}{\int |\psi_1|^2 dv}, \quad H_{22} = \frac{\int \psi_2^* H \psi_2 dv}{\int |\psi_2|^2 dv}$$

and

$$H_{12} = \frac{\int \psi_1^* H \psi_2 dv}{\left[\int |\psi_1|^2 dv \cdot \int |\psi_2|^2 dv\right]^{1/2}}$$

there being no off-diagonal term containing E as a factor, because the wave function $a+b$ is orthogonal to $a-b$.

Let us now abbreviate as follows:

$$i = \int [a(1)]^2 [a(2)]^2 (2/r) dv$$

$$j'' = \int [a(1)]^2 a(2) b(2) (2/r) dv$$

$$H' c(1) d(2) = \left(\frac{2}{R} + \frac{2}{r_{12}} - \frac{2}{a_1} - \frac{2}{a_2} - \frac{2}{b_1} - \frac{2}{b_2} + \frac{2}{c_1} + \frac{2}{d_2}\right) c(1) d(2)$$

$$L = \int H' [a(1)]^2 [a(2)]^2 dv = \frac{2}{R} - 2I + i$$

$$J'' = \int a(1) a(2) H' a(1) b(2) dv = \frac{2}{R} S^{1/2} - S^{1/2} I - I' + j''$$

$$H_{11} = 2E_0 + \frac{2L + 2J + 4K + 8J''}{(2 + 2S^{1/2})^2}$$

$$H_{22} = 2E_0 + \frac{2L + 2J + 4K - 8J''}{(2 - 2S^{1/2})^2}$$

$$H_{12} = \frac{i - j}{2(1 - S)}.$$

It is to be noticed that in addition to the "coulomb" and "exchange" integrals we have a new integral typified by J''. This keeps appearing in the subsequent calculations, and is in general of the same order of magnitude as the other integrals.

$$i = \int [a(1)]^2 [a(2)]^2 (2/r) dv = \lim_{R \to 0} \int [a(1)]^2 [b(2)]^2 (2/r) dv$$

$$= c^4\left\{\frac{8\pi}{\kappa^4}\int a^2 e^{-\kappa a}[\gamma_5(\kappa a)/\kappa a + \Gamma_4(\kappa a)]dv\right\}$$
$$= (\kappa/288)\{24\Gamma_4 - 24\Gamma_4/2^4 - 18\Gamma_5/2^5 - 6\Gamma_6/2^6 - \Gamma_7/2^7\}$$
$$= .3633\kappa.$$

If $\kappa = 1.26$, $\quad i = 6.2$ volts.

This value of i is larger than the ionization potential of lithium, which would indicate a negative electron affinity. No accurate calculations of the electron affinity of lithium have been made.

Calculation of j''

We may calculate j'' in two different ways, and thus obtain a check. The first way is direct, and the second requires the Neumann expansion. Here we give only the first method.

$$j'' = \int (2/r)a(1)b(1)[a(2)]^2 dv$$
$$= (8\pi c^4/\kappa^4)\int abe^{-\kappa(a+b)/2}\{\gamma_5(\kappa a)/\kappa a + \Gamma_4(\kappa a)\}\cdot(2\pi/R)adabdb.$$

Setting $y = \kappa a$,

$$\int_{|R-a|}^{R+a} b^2 dbe^{-\kappa b/2} = (2/\kappa)^3\left\{\Gamma_3\left|\frac{\alpha - y}{2}\right| - \Gamma_3\left(\frac{\alpha + y}{2}\right)\right\}$$

$$j'' = (128\pi^2 c^4/\alpha\kappa^9)\int_0^\infty y^2 dye^{-y/2}\{\gamma_5(y)/y + \Gamma_4(y)\}\left\{\Gamma_3\left|\frac{\alpha - y}{2}\right| - \Gamma_3\left(\frac{\alpha + y}{2}\right)\right\}$$

$$= (128\pi^2 c^4/\alpha\kappa^9)\Big[\int_0^\alpha ydy\{\gamma_5(y) + y\Gamma_4(y)\}e^{-\alpha/2}\cdot\{a_0 - a_1 y + a_2 y^2\}$$
$$+ \int_\alpha^\infty ydye^{-y}\{\gamma_5(y) + y\Gamma_4(y)\}e^{\alpha/2}\cdot\{b_0 + b_1 y + b_2 y^2\}$$
$$- \int_0^\infty ydye^{-y}\{\gamma_5(y) + y\Gamma_4(y)\}e^{-\alpha/2}\{a_0 + a_1 y + a_2 y^2\}\Big]$$

where

$$a_0 = 2 + \alpha + \alpha^2/4 \quad a_1 = 1 + \alpha/2 \quad a_2 = b_2 = \tfrac{1}{4}$$
$$b_0 = 2 - \alpha + \alpha^2/4 \quad b_1 = 1 - \alpha/2.$$

The calculation gives:

$$j'' - I' = -(\kappa/72\alpha)\{2e^{-\alpha/2}(134.01 - 56.531\alpha + 13.3125\alpha^2)$$
$$- 32e^{-\alpha/2}[(\alpha/2)^7(A_6 - 2A_5 + A_4) + (\alpha/2)^6(A_5 - 4A_4 + 3A_3)$$
$$+ (\alpha/2)^5(A_4/2 - 3A_3 + 9A_2/2) + (\alpha/2)^4(3A_3 + 3A_1)$$
$$+ (\alpha/2)^3(3A_2 + 6A_1) + (\alpha/2)^2\cdot 6A_1]_\alpha$$
$$+ 32e^{\alpha/2}[(\alpha/2)^7(A_6 - 2A_5 + A_4) + (\alpha/2)^6(5A_5 - 8A_4 + 3A_3)$$
$$+ (\alpha/2)^5(12.5A_4 - 15A_3 + 4.5A_2) + (\alpha/2)^4(18A_3 - 15A_2 + 3A_1)$$
$$+ (\alpha/2)^3(15A_2 - 6A_1) + (\alpha/2)^2\cdot 6A_1]_{2\alpha}\}$$

where the subscript α after the bracket indicates that the A's inside have α as an argument.

TABLE II.

α	$\alpha=3$	4	5	6	7	8	9	10
j''/κ	0.3155	0.2834	0.2482	0.2124	0.1762	0.1426	0.1132	0.0876
L/κ	.1364	.0589	.0505	.0690	.0946	.1207	.1443	.1643
J''/κ	.0787	−.0204	−.0489	−.0490	−.0413	−.0318	−.0230	−.0167
J/κ	.1098	.0133	−.0159	−.0197	−.0160	−.0110	−.0069	−.0042
K'/κ	.0439	−.0550	−.0782	−.0704	−.0550	−.0373	−.0236	−.0147
$(H_{11}-2E_0)/\kappa$	.0908	−.0181	−.0531	−.0536	−.0412	−.0217	−.0004	+.0188
$(H_{22}-2E_0)/\kappa$	.7888	.6392	.5028	.3972	.3229	.2745	.2331	.2029
H_{12}/κ	.0639	.0679	.0708	.0747	.0786	.0832	.0880	.0928
$^1\Sigma/\kappa$	.0850	−.0250	−.0620	−.0657	−.0574	−.0435	−.0298	−.0194

The $^1\Sigma$ state referred to in Table II is the nonpolar one. It is seen that the two methods (a) and (b) of calculating the molecular constants lead to practically the same results. In what follows, we shall calculate by method (a).

II. Interaction of Two Normal Beryllium Atoms

There is but one possible state for the molecule when the two atoms are each in a ^1S state, and that is the $^1\Sigma$ state. We assume the wave function to be

$$\psi = \sum_P (-)^{\sigma_P} P a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4)$$

where P refers to a permutation of 1, 2, 3, 4 and σ_p is the order of P. The energy is

$$E = \frac{\int \psi^* H \psi dv}{\int \psi^* \psi dv}$$

where

$$H = \sum_{i=1}^{4} \Delta_i + \frac{8}{R} - \sum_{i=1}^{4} \left(\frac{4}{a_i} + \frac{4}{b_i} \right) + \sum_{i<j} \frac{2}{r_{ij}} .$$

Then

$$E = \frac{\int \left[\sum_{P'} (-)^{\sigma_{P'}} P' a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \right] H \left[\sum_{P''} (-)^{\sigma_{P''}} P'' a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \right] dv}{\int \left[\sum_{P'} (-)^{\sigma_{P'}} P' a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \right] \cdot \left[\sum_{P''} (-)^{\sigma_{P''}} P'' a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \right] dv} .$$

Summing over P'', and setting $P = P' P''^{-1}$:

$$E = \frac{\int \left[\sum_{P} (-)^{\sigma_P} P a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \right] H \left[a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \right] dv}{\int \left[\sum_{P} (-)^{\sigma_P} P a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \right] \cdot \left[a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \right] dv} .$$

Splitting off the unperturbed energy,

$$E-E_0=\frac{\int\left[\sum_P(-)^{\sigma_P}Pa_\alpha^*(1)a_\beta^*(2)b_\alpha^*(3)b_\beta^*(4)\right]\cdot H'[a_\alpha(1)a_\beta(2)b_\alpha(3)b_\beta(4)]dv}{\int\left[\sum_P(-)^{\sigma_P}Pa_\alpha^*(1)a_\beta^*(2)b_\alpha^*(3)b_\beta^*(4)\right]\cdot[a_\alpha(1)a_\beta(2)b_\alpha(3)b_\beta(4)]dv}$$

where

$$H'=\frac{8}{R}-\frac{4}{b_1}-\frac{4}{b_2}-\frac{4}{a_3}-\frac{4}{a_4}+\frac{2}{r_{13}}+\frac{2}{r_{14}}+\frac{2}{r_{23}}+\frac{2}{r_{24}}$$
$$=H'(13)+H'(14)+H'(23)+H'(24)$$
$$H'(ij)=\frac{2}{R}-\frac{2}{b_i}-\frac{2}{a_j}+\frac{2}{r_{ij}}.$$

The condition of spin orthogonality gives nonvanishing contributions from $P=1$, (13), (24), (13)(24) only. The contributions to numerator and denominator of the expression for $E-E_0$ are:

P	Numerator	Denominator
1	$4J$	1
$(13)=(24)$	$-K-2S^{1/2}J''-SJ$	$-S$
(13)(24)	$4SK$	S^2.

Then

$$E-E_0=\frac{4(J+SK)-2(K+SJ)-4S^{1/2}J''}{(1-S)^2}.$$

α	$\alpha=3$	4	5	6	7	8	9	10
$^1\Sigma/\kappa$	0.840	0.584	0.392	0.251	0.162	0.099	0.058	0.028

The $^1\Sigma$ state is seen to be a repulsive one.

Discussion

The calculations for lithium show that good results may be obtained with simple wave functions. The success here justifies, we believe, the use of similar functions in the more complicated problems.

One would expect that two normal beryllium atoms would behave toward each other as do two normal helium atoms. This expectation is given support by our calculations, which show that the resulting molecular state is repulsive.

However, it is not at all obvious that two beryllium atoms, one of which is in the normal state, and the other of which is in the first excited state, should repel each other. The character of the states resulting from this configuration will be determined in the concluding installment of this paper, which is to follow shortly.

MANY-ELECTRON WAVE FUNCTIONS

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Abstract

If it is possible to describe the state of an atom by the addition of several vectors, and if one assumes the wave function for any state of a configuration to be a linear combination of product functions for that configuration, then one can determine the coefficients in the linear combination by a simple method. Examples are given. The usual interval formula is not applicable for $2p^3$, where nonsplitting is the case.

Introduction

In A previous paper,[1] the writer has investigated, for two equivalent $2p$ electrons, the stages between (ls), or Russell-Saunders, coupling and (jj) coupling. As a zeroth approximation, the wave functions for the intermediate case were assumed to be linear combinations of product functions associated with $2p^2$. The secular equation could be solved rather readily when the functions used to determined its matrix elements were those linear combinations associated with the various terms (such as $^3P_2$) of Russell-Saunders coupling. Such linear combinations were found by solving an appropriate secular equation. The purpose of the present paper is to call attention to an apparently little-known method which enables one to write down these linear combinations directly.

1. If there exist two independent states $\psi_{m_A}{}^A$ and $\psi_{m_B}{}^B$, which may be represented by vectors A and B with projections m_A and m_B respectively, then the total system may be written as $\psi_{m_A}{}^A\psi_{m_B}{}^B$. If the two vectors combine to form a resultant vector C with projection m_C, then this state will have the form $\psi_{m_C}{}^C=\Sigma_{m_Am_B}S_{Cm_Am_B}{}^{AB}\psi_{m_A}{}^A\psi_{m_B}{}^B$, where $m_A+m_B=m_C$. The coefficients $S_{Cm_Am_B}{}^{AB}$ are known,[2] at least if we restrict the quantum numbers to integral and half-integral values. If $\psi_{m_A}{}^A$ refer to electrons 1 and 2, and $\psi_{m_B}{}^B$ to electron 3, the resulting function will not be antisymmetric with respect to interchange of any two electrons, in general, and determinant wave functions must be constructed.

For convenience, the coefficients for $B=\frac{1}{2}$ and $B=1$ are listed.

Table I. $S_{Cm_Am_B}{}^{A\frac{1}{2}}$

C	$m_B=-\frac{1}{2}$	$m_B=\frac{1}{2}$
$A-\frac{1}{2}$	$\left(\frac{A+m_C+\frac{1}{2}}{2A+1}\right)^{1/2}$	$-\left(\frac{A-m_C+\frac{1}{2}}{2A+1}\right)^{1/2}$
$A+\frac{1}{2}$	$\left(\frac{A-m_C+\frac{1}{2}}{2A+1}\right)^{1/2}$	$\left(\frac{A+m_C+\frac{1}{2}}{2A+1}\right)^{1/2}$

[1] J. H. Bartlett, Jr., Phys. Rev. **34,** 1252 (1929). See also Phys. Rev. **35,** 229 (1930).
[2] E. Wigner, Gruppentheorie (Vieweg, 1931) S. 206.

TABLE II. $S^{A1}_{C m_A m_B}$

C	$m_B=-1$	$m_B=0$	$m_B=1$
$A-1$	$\left[\frac{(A+m_C)(A+m_C+1)}{2A(2A+1)}\right]^{1/2}$	$-\left[\frac{(A+m_C)(A-m_C)}{A(2A+1)}\right]^{1/2}$	$\left[\frac{(A-m_C+1)(A-m_C)}{2A(2A+1)}\right]^{1/2}$
A	$\left[\frac{(A-m_C)(A+m_C+1)}{2A(A+1)}\right]^{1/2}$	$\frac{m_C}{[A(A+1)]^{1/2}}$	$-\left[\frac{(A-m_C+1)(A+m_C)}{2A(A+1)}\right]^{1/2}$
$A+1$	$\left[\frac{(A-m_C)(A-m_C+1)}{(2A+1)(2A+2)}\right]^{1/2}$	$\left[\frac{(A+m_C+1)(A-m_C+1)}{(2A+1)(A+1)}\right]^{1/2}$	$\left[\frac{(A+m_C+1)(A+m_C)}{(2A+1)(2A+2)}\right]^{1/2}$

Table II has been given in a different form by Wigner.[3] The form above seems to be handier and more symmetrical.

2. A simple example is that of two equivalent p electrons. Let the wave function $\psi_{m_A}{}^{(1)}\psi_{m_B}{}^{(2)}$ be denoted by (m_A, m_B). We shall determine the space function by combining the l-vectors, and the spin function by combining the s-vectors. The product of these two functions will then be represented by a vector L and a vector S, together with their projections m_L and m_S. It will be a linear combination of individual product functions and need not have the required antisymmetry property. If, however, we replace each individual product function by the corresponding determinant, the linear combination of these determinants will be our required function. In the case of two electrons, $S_1=\frac{1}{2}$ and $S_2=\frac{1}{2}$, resulting in wave functions symmetric or antisymmetric in the spins. The space factor turns out likewise, and so we do not need to introduce determinant functions. This is only a special case, however.

The space factors for $2p^2$, $m_l=0$ follow:[4]

$$S:(\tfrac{1}{3})^{1/2}\{(1,-1)-(0,0)+(-1,1)\}$$
$$D:(\tfrac{1}{6})^{1/2}\{(1,-1)+2(0,0)+(-1,1)\}$$
$$P:(\tfrac{1}{2})^{1/2}\{(1,-1)-(-1,1)\}.$$

Since these are either symmetric or antisymmetric in the two electrons, it is only necessary to multiply by the appropriate spin factor to obtain a wave function which is antisymmetric.

For $m_l=1$, $P:(\tfrac{1}{2})^{1/2}\{(1,0)-(0,1)\}$
$D:(\tfrac{1}{2})^{1/2}\{(1,0)+(0,1)\}$.

For $m_l=-1$, $P:(\tfrac{1}{2})^{1/2}\{(0,-1)-(-1,0)\}$
$D:(\tfrac{1}{2})^{1/2}\{(0,-1)+(-1,0)\}$.

The spin functions are:

$$s=0:(\tfrac{1}{2})^{1/2}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}$$

[3] E. Wigner, Gruppentheorie, p. 208.

[4] These functions agree with those in the previous paper, reference 1.

$$s = 1 \begin{cases} m_s = 1 : \alpha(1)\alpha(2) \\ m_s = 0 : (\tfrac{1}{2})^{1/2}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\} \\ m_s = -1 : \beta(1)\beta(2). \end{cases}$$

$\alpha(1)$ denotes that function of electron 1 corresponding to $m_s = \frac{1}{2}$, and $\beta(1)$ corresponds to $m_s = -\frac{1}{2}$.

If now, we wish the functions for ^3P, $j = 0$, 1, and 2, then the coefficients $S^{1\,1}{}_{j\,m_l m_s}$ are what are required. For $m = 0$ (and for the other values of m also) the form of the wave function is the same as for $m_l = 0$ above,[4] i.e.:

$$^3P_0 : (\tfrac{1}{3})^{1/2}\{(1, -1) - (0, 0) + (-1, 1)\}.$$

The parentheses refer here to m_l and m_s however, instead of to m_{l_1} and m_{l_2}.

3. A more complicated example is furnished by the configuration $2p^3$ which has for terms ^2P, ^2D, and ^4S. When there are three electrons described by vectors l_1, l_2, l_3 and s_1, s_2, s_3 then we may suppose the resultant of l_1 and l_2 to be $\bar{l}$ and that of s_1 and s_2 to be $\bar{s}$. The total wave function characteristic of a state (l, s, m_l, m_s) may be written as

$$\sum_p (-)^{i_p} P \psi^{l}_{m_l} \psi^{s}_{m_s} = \sum s_{\bar{l}}(\bar{l}l_3; \bar{m}_l m_{l_3}) s_{\bar{s}}(\bar{s}s_3; \bar{m}_s m_{s_3}) \sum (-)^{i_p} P$$
$$[s_{\bar{l}}(l_1 l_2; m_{l_1} m_{l_2}) s_{\bar{s}}(s_1 s_2; m_{s_1} m_{s_1}) \psi(l_1 s_1; m_{l_1} m_{s_1}/1)$$
$$\psi(l_2 s_2; m_{l_2} m_{s_2}/2)]\psi(l_3 s_3; m_{l_3} m_{s_3}/3)$$

where P is a permutation of (123) and i_p its order. Thus we may proceed from determinant wave functions for two electrons, if it proves to be convenient. If we try to build up the $^2D_{5/2}$, $m_l = 2$ from $2p^2\ ^1D_2$ and $2p$ then the functions for ^1D are:

$$m_l = 2 \qquad (\tfrac{1}{2})^{1/2} \left| \alpha^1(1)\beta^1(2) \right|$$
$$m_l = 1 \qquad (\tfrac{1}{2}) \left\{ \left| \alpha^1(1)\beta^0(2) \right| - \left| \alpha^0(1)\beta^1(2) \right| \right\}.$$

For $2p$,

$$m_l = 0 \qquad \alpha^0(3)$$
$$m_l = 1 \qquad \alpha^1(3)$$

(where the superscripts now denote the magnetic quantum number).

The only possible function for $^2D_{5/2}$, $m_l = 2$ is then $(1/6)^{1/2}\left|\alpha^1(1)\beta^1(2)\alpha^0(3)\right|$. One does not need to resort to the vector addition method to deduce this result.

For $j = 3/2$, $m = 3/2$ there are three possible states, namely ^2D, ^2P, and ^4S. The ^2D may be considered as arising from $2p\ ^3P$ and $2p$, or else from $2p^2\ ^1D$ and $2p$. The same wave function is obtained in either case, which seems at first surprising because the ^1D and ^3P terms have not the same energy. But if we consider that the added electron is equivalent to the other two, the reason is apparent. If a nonequivalent p electron should be added, then we should obtain two ^2D terms with different energies.

For $2p^3$ some of the wave functions follow:

$$^2D: m_l = 1,\ m_s = \tfrac{1}{2}: (1/12)^{1/2}\{\,|\,\beta^1(1)\alpha^{-1}(2)\alpha'(3)\,| - |\,\beta^0(1)\alpha^1(2)\alpha^0(3)\,|\,\}$$

$$m_l = 0,\ m_s = \tfrac{1}{2}: (1/6)\{\,|\,\beta^1(1)\alpha^{-1}(2)\alpha^0(3)\,| + 2|\,\beta^0(1)\alpha^{-1}(2)\alpha^1(3)\,| + |\,\beta^{-1}(1)\alpha^0(2)\alpha^1(3)\,|\,\}$$

$$^2P: m_l = 1\quad m_s = \tfrac{1}{2}: (1/12)^{1/2}\{\,|\,\beta^1(1)\alpha^{-1}(2)\alpha^1(3)\,| + |\,\beta^0(1)\alpha^1(2)\alpha^0(3)\,|\,\}$$

$$m_l = 0\quad m_s = \tfrac{1}{2}: (1/12)^{1/2}\{\,|\,\beta^1(1)\alpha^{-1}(2)\alpha^0(3)\,| + |\,\beta^{-1}(1)\alpha^1(2)\alpha^0(3)\,|\,\}$$

$$^4S: m_l = 0\quad m_s = 3/2: (1\ 6)^{1/2}\,|\,\alpha^1(1)\alpha^0(2)\alpha^{-1}(3)\,|$$

$$m_l = 0\quad m_s = \tfrac{1}{2}: (1/18)^{1/2}\{\,|\,\beta^{-1}(1)\alpha^1(2)\alpha^0(3)\,| + |\,\beta^0(1)\alpha^{-1}(2)\alpha^1(3)\,| + |\,\beta^1(1)\alpha^0(2)\alpha^{-1}(3)\,|\,\}$$

$$^2D_{3/2}, m = 3/2: (1/6)^{1/2}\{(4/5)^{1/2}\,|\,\alpha^1(1)\beta^1(2)\beta^0(3)\,| - (1/10)^{1/2}\,|\,\alpha^1(1)\beta^1(2)\alpha^{-1}(3)\,| + (1/10)^{1/2}\,|\,\beta^0(1)\alpha^1(2)\alpha^0(3)\,|\,\}$$

$$^2P_{3/2},\ m = 3/2: (1/12)^{1/2}\{\,|\,\alpha^1(1)\beta^1(2)\alpha^{-1}(3)\,| + |\,\alpha^0(1)\beta^0(2)\alpha^1(3)\,|\,\}.$$

4. Suppose now, to verify the correctness of the linear combinations, that we calculate the energy levels of $2p^3$, $j=3/2$, for (jj) coupling. This necessitates finding the matrix elements of $(l\cdot s)_1+(l\cdot s)_2+(l\cdot s)_3$. Given two determinantal wave functions $|n_1(1)\ n_2(2)\ n_3(3)|$ and $|n_1'(1)\ n_2'(2)\ n_3'(3)|$, then the matrix elements will not vanish only when not more than one of the n's is different from an n'. If $n_1=n_1'$, $n_2=n_2'$ and $n_3\neq n_3'$, the matrix element is $(n_3|l\cdot s|n_3')$. If $n_3=n_3'$, the matrix element is $(n_1|l\cdot s|n_1')+(n_2|l\cdot s|n_2')+(n_3|l\cdot s|n_3')$.

The matrix elements of $(l\cdot s)$ are:[5]

$$(m_s, m_l|\ l\cdot s\ |\ m_s, m_l) = \lambda m_s m_l$$

$$(\alpha, m_l|\ l\cdot s\ |\ \beta, m_l+1) = (\lambda/2)[l(l+1) - m_l(m_l+1)]^{1/2}$$

$$(\beta, m_l|\ l\cdot s\ |\ \alpha, m_l-1) = (\lambda/2)[l(l+1) - m_l(m_l-1)]^{1/2}.$$

The secular equation is then:

$$\begin{vmatrix} -\epsilon & (5/4)^{1/2} & 0 \\ (5/4)^{1/2} & -\epsilon & 1 \\ 0 & 1 & -\epsilon \end{vmatrix} = 0.$$

The roots are $\epsilon=0$ and $\pm 3/2$, agreeing with what one would expect from elementary considerations. When the electrostatic interaction is not negligible, then one must solve the cubic equation by applying the well-known formulae.

It is seen that the diagonal terms in the matrix of (l.s) are zero, which means that the ^2P and ^2D of $2p^3$ do not split up, as is the case[1] with $2s2p^3$. This is not what one should expect from the formula $\Delta E=\text{const.}\,[j(j+1)-l(l+1)-s(s+1)]$, showing that the range of applicability of this formula is limited. One can verify the fact that no splitting occurs by a consideration of $^2D_{5/2}$ and $^2P_{1/2}$. The displacement must be the same for (ls) coupling as for (jj)

[5] W. Heisenberg u. P. Jordan, Zeits. f. Physik **37**, 268 (1926).

coupling, where it is zero, a result that one can obtain without using wave functions.

Discussion

The vectorial method of finding correct linear combinations seems to be quite general, but does not, of course, apply when the resulting state cannot be represented as a vector which is the sum of several component vectors. For instance, the transition from (*ls*) to (*jj*) coupling involves a disturbance of symmetry so that one cannot find the wave functions for the intermediate cases by the above method. But it becomes much easier to find these functions if one knows the proper functions for (*ls*) coupling. The problem reduces to that of solving a secular equation for a given j and m, the degree of this equation being the only practical limitation, instead of the number of electrons.

Note added Sept. 8, 1931: The correct linear combinations can also be found by a method due to N. M. Gray and N. A. Wills (Phys. Rev. **38,** 248, 1931). The present writer believes, however, that the vectorial method, due to Wigner, is the simpler.

SPECTRA OF TWO ELECTRON SYSTEMS

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Abstract

Following the method of Güttinger and Pauli[1] four angular momentum vectors are treated in matrix mechanics. Analytic formulas are obtained for the matrix components of the spin-orbit interaction of two electrons in LS coupling. Since the electrostatic energy in LS coupling is a diagonal matrix whose elements may be calculated by Slater's method, this gives the complete energy matrix. Then for any two electron configuration one easily obtains the secular equations whose roots give the energy levels in intermediate coupling. In this manner the secular equations are worked out for the configurations p^2, $p \cdot p$, d^2, $d \cdot d$, and $d \cdot p$.

Introduction

In THE theory of complex spectra the effect of the electrostatic repulsion of the electrons on the energy levels of an atom has been reduced in many cases to the calculation of a few radial integrals.[2] By this method it is always possible to calculate the multiplet separations for two electron configurations with such accuracy as is afforded by a first order perturbation theory. In order to obtain more detailed information about the energy levels it is necessary to include in the perturbation problem the interaction of the spin each electron with its own orbital motion. This has been done for two electrons when one is in an s state.[3] Also partial information (in some simple cases complete) about the secular equations has been obtained by Goudsmit.[4]

It is easy to see why the spin-orbit interaction has not been dealt with by Slater's method. In this method it is not necessary to find the wave function for a given state of the atom. For due to the high degree of degeneracy remaining in the problem after the application of the perturbation, it is possible to find all the energy levels from the invariance of diagonal sums. When the spin-orbit interaction is included, much of this degeneracy is removed so the diagonal sum method loses its effectiveness.

The essential difficulty with Slater's wave functions is that the square of the total angular momentum, J^2, which is an integral of the equations of motion, is not diagonal when these wave functions are used. Consequently the secular determinant when computed with these functions, is not factored according to J values as it should be. The proper linear combination of Slater's functions to make J^2 diagonal may be found by studying the angular momentum operators.[5] With these proper functions as a basis the matrix of the spin-

[1] Güttinger and Pauli, Zeits. f. Physik **67,** 743 (1931). This will be referred to as 1.

[2] J. C. Slater, Phys. Rev. **34,** 1293 (1929).

[3] Houston, Phys. Rev. **33,** 297 (1929).

[4] Goudsmit, Phys. Rev. **35,** 1325 (1930). This method has recently been extended by D.R Inglis, Phys. Rev. **38,** 862 (1931).

[5] Gray and Wills, Phys. Rev. **38,** 248 (1931).

orbit interaction would be factored according to J values. However for the general two electron configuration this appears to be a lengthy process. So in this paper we attempt to calculate the spin-orbit interaction in LS coupling directly from the matrix equations.[6]

Elimination of the Quantum Number M_J

If $\boldsymbol{L}$ is the total orbital angular momentum, $\boldsymbol{S}$ is the total spin angular momentum and $\boldsymbol{J}$ their resultant, then

$$\begin{aligned} \boldsymbol{J} &= \boldsymbol{L} + \boldsymbol{S} \\ \boldsymbol{L} &= \boldsymbol{l}_1 + \boldsymbol{l}_2 \\ \boldsymbol{S} &= \boldsymbol{s}_1 + \boldsymbol{s}_2 \end{aligned} \tag{1}$$

where $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$ are the orbital and $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$ are the spin angular momenta of electrons 1 and 2 respectively. Then the following commutation relations are valid

$$\begin{aligned} [J_z, A_z] &= 0 \\ [J_z, A_y] &= [A_z, J_y] = iA_z \\ [J_z, B] &= 0 \end{aligned} \tag{2}$$

where $\boldsymbol{A}$ is any vector which is a function of the spin and orbital momentum vectors and B is any scalar formed from these vectors. In these equations angular momentum is measured in units of $h/2\pi$. In particular Eqs. (2) hold for $\boldsymbol{l}_1$, $\boldsymbol{l}_2$, $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$. Now we suppose that J^2 is diagonal with the characteristic values $J(J+1)$ and J_z is a diagonal with the characteristic values M_J, $|M_J| \leqq J$. Then from reference 1 we find that the solutions of Eqs. (2) are

$$\begin{aligned} (A_x \pm iA_y)^{JM_J}_{JM_J\mp 1} &= A^J_J \{(J \pm M_J)(J \mp M_J + 1)\}^{1/2} \\ A^{JM_J}_{zJM_J} &= A^J_J M_J \\ (A_x \pm iA_y)^{J\ M_J}_{J+1M_J\mp 1} &= A^J_{J+1}(\pm 1)\{(J \mp M_J + 1)(J \mp M_J + 2)\}^{1/2} \\ A^{J\ M_J}_{zJ+1M_J} &= A^J_{J+1}\{(J+1)^2 - M_J{}^2\}^{1/2} \\ (A_x \pm iA_y)^{J\ M_J}_{J-1M_J\mp 1} &= A^J_{J-1}(\mp 1)\{(J \pm M_J)(J \pm M_J - 1)\}^{1/2} \\ A^{J\ MJ}_{zJ+1M_J} &= A^J_{J-1}(J^2 - M_J{}^2)^{1/2}. \end{aligned} \tag{3}$$

In particular if $\boldsymbol{A} = \boldsymbol{J}$, then $A^J_J = 1$ and $A^J_{J+1} = 0$.

Calculation of $\boldsymbol{L}$ and $\boldsymbol{S}$

The calculation of $\boldsymbol{S}$ is exactly the same as in reference 1. We now suppose that L^2 and S^2 are also diagonal with the characteristic values $L(L+1)$ and

[6] We should also note another possible method of obtaining the matrix of the spin-orbit interaction by those famous ξ's and η's, which may be simple for one experienced in their peculiarities. H. Weyl, Gruppentheorie und Quantenmechanick Kap. III; H. A. Kramers, Amst. Akad. **33,** 953 (1930).

$S(S+I)$. This is possible since the matrices L^2, S^2, J^2 and J_z all commute with one another. Then from reference 1 we find for $\boldsymbol{S}$

$$S_J^J = \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

$$S_{J-1}^J = \left(\frac{(L+S+1-J)(L+S+1+J)(J-L+S)(J-S+L)}{4J^2(2J-1)(2J+1)}\right)^{1/2} \tag{4}$$

$$S_{J-1}^J = S_J^{J-1}.$$

The last equation follows from the Hermitean character of the components of $\boldsymbol{S}$.

The results for $\boldsymbol{L}$ may be obtained from the above by interchanging L and S. This gives

$$L_J^J = \frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)}$$

$$L_{J-1}^J = -\left(\frac{(S+L+1-J)(S+L+1+J)(J-S+L)(J-L+S)}{4J^2(2J-1)(2J+1)}\right)^{1/2} \tag{5}$$

$$L_{J-1}^J = L_J^{J-1}.$$

The minus sign before the component nondiagonal in J occurs in extracting a square root. The minus sign must be used in order that $(L_x+S_x)^{LSJ}_{LSJ\pm1}{}^{M_J}_{M_J}=0$ as is required by the fact that J^2 commutes with all components of J. Of course all components of $\boldsymbol{L}$ and $\boldsymbol{S}$ are diagonal in L and S as all components of both $\boldsymbol{L}$ and $\boldsymbol{S}$ commute with L^2 and S^2.

Dependence of l_1, l_2, s_1 and s_2 on the Quantum Number J

In the following formulas we use l for l_1 and l_2 and s for s_1 and s_2 whenever the formulas apply for both subscripts. We find the dependence of $\boldsymbol{l}$ on J from the equation

$$[S_x - iS_y, l_z]^{L\ SJ'\ M_J}_{L'SJ''M_J+1} = 0.$$

The calculation is exactly the same as the calculation of the coordinate matrix in reference 1. Hence we have the result

$$l_{LSJ}^{LSJ} = l_{LS}^{LS}\frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)}$$

$$l_{LSJ+1}^{LSJ} = -l_{LS}^{LS}\left(\frac{(L+S+J+2)(L+S-J)(J+1+L-S)(J+1-L+S)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l_{L-1SJ+1}^{L\ SJ} = -l_{L-1S}^{L\ S}\left(\frac{(J-L+S+2)(J-L+S+1)(L+S-1-J)(L+S-J)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} \tag{6}$$

$$l_{L-1SJ}^{L\ SJ} = l_{L-1S}^{L\ S}\left(\frac{(J+L-S)(J-L+S+1)(L+S+1+J)(L+S-J)}{4J^2(J+1)^2}\right)^{1/2}$$

$$l_{L-1SJ-1}^{L\ SJ} = l_{L-1S}^{L\ S}\left(\frac{(J+L-S-1)(J+L-S)(L+S+1+J)(L+S+J)}{4J^2(2J-1)(2J+1)}\right)^{1/2}.$$

The remaining terms may be obtained by interchanging the upper and lower indices.

For the dependence of s on J we use the equation

$$[L_x - iL_y, s_z]^{LS\,J'\,M_J}_{LS'J''M_J+1} = 0.$$

With $J'=J-1$ and $J''=J+1$ we have

$$L^{LSJ-1}_{LSJ}\quad s^{LS\,J}_{LS'J+1} = s^{LSJ-1}_{LS'J}\,L^{LS'J}_{LS'J+1}. \tag{7}$$

With $J'=J$, $J''=J+1$ and with $J'=J$, $J''=J-1$ we obtain the following two equations in exactly the same manner as Eqs. (15′) and (16′) are obtained in reference 1.

$$\{(J+1)L^{LSJ}_{LSJ} - (J+2)L^{LS'J+1}_{LS'J+1}\}s^{LS\,J}_{LS'J+1} - L^{LS'J}_{LS'J+1}s^{LS\,J}_{LS'J} = 0 \tag{8}$$

$$\{JL^{LSJ}_{LSJ} - (J-1)L^{LS'J-1}_{LS'J-1}\}s^{LS\,J}_{LS'J-1} + L^{LS'J}_{LS'J-1}s^{LS\,J}_{LS'J} = 0. \tag{9}$$

With $S'=S$ in Eq. (7) we obtain

$$s^{LSJ}_{LSJ+1} = -\,s^{LS}_{LS}L^{LSJ}_{LSJ+1}$$

$$= s^{LS}_{LS}\left(\frac{(L+S-J)(L+S+J+2)(J+1+L-S)(J+1+S-L)}{4(J+1)^2(2J-1)(2J+1)}\right)^{1/2} \tag{10a}$$

From Eq. (8) with $S'=S$ we have

$$s^{LSJ}_{LSJ}L^{LSJ}_{LSJ+1} = s^{LSJ}_{LSJ+1}\{(J+1)L^{LSJ}_{LSJ} - (J+2)L^{LSJ+1}_{LSJ+1}\}$$

$$s^{LSJ}_{LSJ} = s^{LS}_{LS}\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \tag{10b}$$

From Eq. (7) with $S'=S-1$ we have

$$L^{LSJ-1}_{LSJ}\;s^{LS\;\;J}_{LS-1J+1} = s^{LS\;\;J-1}_{LS-1J}\quad L^{LS-1J}_{LS-1J+1}$$

or

$$\left(\frac{(L+S+1-J)(J-S+L)}{4J^2(2J-1)(2J+1)}\right)^{1/2} s^{LS\;\;J}_{LS-1J+1}$$

$$= \left(\frac{(L+S-J-1)(J-S+L+2)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} s^{LS\;\;J-1}_{LS-1J}$$

$$s^{LS\;\;J}_{LS-1J+1} = -\,s^{LS}_{LS-1}\left(\frac{(L+S-J-1)(L+S-J)(J-S+L+2)(J-S+L+1)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2} \tag{10c}$$

From Eq. (8) with $S'=S-1$ we have

$$s^{LS\;\;J}_{LS-1J}\,L^{LS-1J}_{LS-1J+1} = s^{LS\;\;J}_{LS-1J+1}\{(J+1)L^{LSJ}_{LSJ} - (J+2)L^{LS-1J+1}_{LS-1J+1}\}$$

$$s^{LS\;\;J}_{LS-1J} = -\,s^{LS}_{LS-1}\left(\frac{(L+S-J)(J-S+L+1)(J+S-L)(L+S+J+1)}{4J^2(J+1)^2}\right)^{1/2} \tag{10d}$$

Finally from Eq. (9) with $S'=S-1$ we obtain

$$s^{LS\ J}_{LS-1J-1} = s^{LS}_{LS-1}\left(\frac{(L+S+J)(J-L+S-1)(J+S-L)(L+S+J+1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}. \quad (10e)$$

The remaining components may be obtained by interchanging the upper and lower indices. Formulas (10a) to (10e) can, except for sign, be obtained from Eqs. (6) by interchanging L and S.

Determination of l^{LS}_{LS} etc.

If we suppose that L^2, S^2, L_z and S_z are diagonal, then $\boldsymbol{L}$, $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$ will be related to each other in the same manner as $\boldsymbol{J}$, $\boldsymbol{L}$ and $\boldsymbol{S}$ in the above calculation. $\boldsymbol{S}$, $\mathbf{s}_1$, and $\mathbf{s}_2$ will also be related in this manner. Then we can obtain the components of $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$ and of $\mathbf{s}_1$ and $\mathbf{s}_2$ in this representation by a substitution of the appropriate quantum numbers in Eqs. (4) and (5). Now suppose we make a unitary transformation to a representation in which J^2, L^2, S^2 and J_z are diagonal. Such a transformation leaves L^2, S^2 and J_z invariant and so can only have components between states of the same L, S and M_J values. Between two sets of L, S and M_J values, the matrix components of $\boldsymbol{l}$ and $\mathbf{s}$ will have a constant factor $l^{L'S}_{L'S}$ and $s^{LS}_{LS'}$. This factor which is determined by the substitution of the appropriate quantum numbers in Eqs. (4) and (5), will not depend on J and will remain after the transformation. The other factor will depend on J and is just the factor we have determined above. Hence we have

$$\begin{aligned}
l^{LS}_{1LS} &= \frac{L(L+1)+l_1(l_1+1)-l_2(l_2+1)}{2L(L+1)} \\
l^{LS}_{2LS} &= \frac{L(L+1)+l_2(l_2+1)-l_1(l_1+1)}{2L(L+1)} \\
l^{L\ S}_{1L-1S} &= \left(\frac{(l_1+l_2-L+1)(l_1+l_2+L+1)(L-l_1+l_2)(L-l_2+l_1)}{4L^2(2L-1)(2L+1)}\right)^{1/2} = -\,l^{L\ S}_{2L-1S} \\
s^{LS}_{1LS} &= \frac{S(S+1)+s_1(s_1+1)-s_2(s_2+1)}{2S(S+1)} \\
s^{LS}_{2LS} &= \frac{S(S+1)+s_2(s_2+1)-s_1(s_1+1)}{2S(S+1)} \\
s^{LS}_{1LS-1} &= \left(\frac{(s_1+s_2-S+1)(s_1+s_2+S+1)(S-s_1+s_2)(S-s_2+s_1)}{4S^2(2S-1)(2S+1)}\right)^{1/2} = -\,s^{LS}_{2LS-1}.
\end{aligned} \quad (11)$$

Remembering that in our case $s_1=s_2=\frac{1}{2}$, the formulas for s_1 and s_2 reduce to

$$\begin{aligned}
s^{LS}_{1LS} &= s^{LS}_{2LS} = \tfrac{1}{2} \\
s^{LS}_{1LS-1} &= -\,s^{LS}_{2LS-1} = \tfrac{1}{2}\left(\frac{(2+S)(2-S)}{(2S-1)(2S+1)}\right)^{1/2}.
\end{aligned}$$

Summary of Formulas

$$(l_x \pm il_y)^{L\,S\,JM_J}_{L'S'JM_J\mp1}/l^{L\,S\,J}_{L'S'J} = (s_x \pm is_y)^{L\,S\,JM_J}_{L'S'JM_J\mp1}/s^{L\,S\,J}_{L'S'J}$$
$$= \{(J \pm M_J)(J \mp M_J + 1)\}^{1/2}$$
$$l_z{}^{L\,S\,JM_J}_{L'S'JM_J}/l^{L\,S\,J}_{L'S'J} = {}^{L\;S\,JM_J}_{z\,L'S'JM_J}/s^{L\,S\,J}_{L'S'J} = M_J$$
$$(l_x \pm il_y)^{L\,S\,J\;\;M_J}_{L'S'J+1M_J\mp1}/l^{L\,S\,J}_{L'S'J+1} = (s_x \pm is_y)^{L\,S\,J\;\;M_J}_{L'S'J+1M_J\mp1}/s^{L\,S\,J}_{L'S'J+1}$$
$$= \pm\{(J \mp M_J + 1)(J \mp M_J + 2)\}^{1/2}$$

$$l_z{}^{LSJ\;\;M_J}_{L'S'J+1M_J}/l^{L\,S\,J}_{L'S'J+1} = {}^{L\,S\,J\;\;M_J}_{z\,L'S'J+1M_J}/s^{L\,S\,J}_{L'S'J+1} = \{(J+1)^2 - M_J{}^2\}^{1/2}$$
$$(l_x \pm il_y)^{LSJ\;\;M_J}_{L'S'J-1M_J\mp1}/l^{L\,S\,J}_{L'S'J-1} = (s_x \pm is_y)^{L\,S\,J\;\;M_J}_{L'S'J-1M_J\mp1}/s^{L\,S\,J}_{L'S'J-1}$$
$$= \mp\{(J \pm M_J)(J \pm M_J - 1)\}^{1/2}$$
$$l_z{}^{L\,S\,J\;\;M_J}_{L'S'J-1M_J}/l^{L\,S\,J}_{L'S'J-1} = {}^{L\,S\,J\;\;M_J}_{z\,L'S'J-1M_J}/s^{L\,S\,J}_{L'S'J-1} = (J^2 - M_J{}^2)^{1/2}$$

$$l^{LSJ}_{LSJ+1}/l^{LS}_{LS} = -\left(\frac{(L+S+J+2)(L+S-J)(J+1+L-S)(J+1+S-L)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l^{LSJ}_{LSJ}/l^{LS}_{LS} = \frac{J(J+1) - S(S+1) + L(L+1)}{2J(J+1)}$$

$$l^{LSJ}_{LSJ-1}/l^{LS}_{LS} = -\left(\frac{(L+S+J+1)(L+S+1-J)(J+L-S)(J+S-L)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$l^{L\;\;SJ}_{L-1SJ+1}/l^{L\;\;S}_{L-1S} = -\left(\frac{(L+S-J-1)(L+S-J)(J-L+S+2)(J-L+S+1)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l^{L\;\;SJ}_{L-1SJ}/l^{L\;\;S}_{L-1S} = \left(\frac{(L+S-J)(J-L+S+1)(J+L-S)(L+S+J+1)}{4J^2(J+1)^2}\right)^{1/2}$$

$$l^{L\;\;SJ}_{L-1SJ-1}/l^{L\;\;S}_{L-1S} = \left(\frac{(L+S+J)(J+L-S-1)\,(J+L-S)(L+S+J+1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$l^{L\;\;SJ}_{L+1SJ+1}/l^{L\;\;S}_{L+1S} = \left(\frac{(L+S+J+2)(J+L-S+1)(J+L-S+2)(L+S+J+3)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$l^{L\;\;SJ}_{L+1SJ}/l^{L\;\;S}_{L+1S} = \left(\frac{(L+S-J+1)(J-L+S)(J+L-S+1)(L+S+J+2)}{4J^2(J+1)^2}\right)^{1/2}$$

$$l^{L\;\;SJ}_{L+1SJ-1}/l^{L\;\;S}_{L+1S} = -\left(\frac{(L+S-J+1)(L+S-J+2)(J-L+S)(J-L+S-1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$s^{LSJ}_{LSJ+1}/s^{LS}_{LS} = \left(\frac{(L+S-J)(L+S+J+2)(J+1+L-S)(J+1-L+S)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$s^{LSJ}_{LSJ}/s^{LS}_{LS} = \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$s^{LSJ}_{LSJ-1}/s^{LS}_{LS} = \left(\frac{(L+S-J+1)(L+S+J+1)(J+L-S)(J-L+S)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$s^{LS\ J}_{LS-1J+1}/s^{LS}_{LS-1} = -\left(\frac{(L+S-J-1)(L+S-J)(J-S+L+2)(J-S+L+1)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$s^{LS\ J}_{LS-1J}/s^{LS}_{LS-1} = -\left(\frac{(L+S-J)(J-S+L+1)(J+S-L)(L+S+J+1)}{4J^2(J+1)^2}\right)^{1/2}$$

$$s^{LS\ J}_{LS-1J-1}/s^{LS}_{LS-1} = \left(\frac{(L+S+J)(J-L+S-1)(J+S-L)(L+S+J+1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$s^{LS\ J}_{LS+1J+1}/s^{LS}_{LS+1} = \left(\frac{(L+S+J+2)(J-L+S+1)(J+S-L+2)(L+S+J+3)}{4(J+1)^2(2J+1)(2J+3)}\right)^{1/2}$$

$$s^{LS\ J}_{LS+1J}/s^{LS}_{LS+1} = -\left(\frac{(L+S-J+1)(J-S+L)(J+S-L+1)(L+S+J+2)}{4J^2(J+1)^2}\right)^{1/2}$$

$$s^{LS\ J}_{LS+1J-1}/s^{LS}_{LS+1} = -\left(\frac{(L+S-J+1)(L+S-J+2)(J-S+L)(J-S+L-1)}{4J^2(2J-1)(2J+1)}\right)^{1/2}$$

$$l^{LS}_{1LS} = \frac{L(L+1)+l_1(l_1+1)-l_2(l_2+1)}{2L(L+1)} \qquad l^{LS}_{2LS} = \frac{L(L+1)+l_2(l_2+1)-l_1(l_1+1)}{2L(L+1)}$$

$$l^{L\ S}_{1L-1S} = -\,l^{L\ S}_{2L-1S} = \left(\frac{(l_1+l_2-L+1)(l_1+l_2+L+1)(L-l_1+l_2)(L-l_2+l_1)}{4L^2(2L-1)(2L+1)}\right)^{1/2}$$

$$l^{L\ S}_{1L+1S} = -\,l^{L\ S}_{2L+1S} = \left(\frac{(l_1+l_2-L)(l_1+l_2+L+2)(L+1-l_1+l_2)(L+1-l_2+l_1)}{4(L+1)^2(2L+1)(2L+3)}\right)^{1/2}$$

$$s^{LS}_{1LS}\ s^{LS}_{2LS} = \tfrac{1}{2}$$

$$s^{LS}_{1LS-1} = -\,s^{LS}_{2LS-1} = \tfrac{1}{2}\left(\frac{(2-S)(2+S)}{(2S-1)(2S+1)}\right)^{1/2}$$

$$s^{LS}_{1LS+1} = -\,s^{LS}_{2LS+1} = \tfrac{1}{2}\left(\frac{(1-S)(3+S)}{(2S+1)(2S+3)}\right)^{1/2}$$

The Matrix of the Spin-Orbit Interaction

We wish to obtain the matrix of $a_1(\mathbf{l}_1\cdot\mathbf{s}_1)+a_2(\mathbf{l}_2\cdot\mathbf{s}_2)$. From Eqs. (2) we know that this expression commutes with J^2 and J_z. It will therefore be diagonal with respect to the quantum numbers J and M_J. By matrix multiplication we have

$$\begin{aligned}(\mathbf{l}\cdot\mathbf{s})^{L\ S\ JM_J}_{L'S'JM_J} &= \sum_{J''}\tfrac{1}{2}(l_x-il_y)^{L\ SJ\ \ M_J}_{L'SJ''M_J+1}(s_x+is_y)^{L'S\ J''M_J+1}_{L'S'J\ \ M_J}\\ &\quad+\tfrac{1}{2}(l_x+il_y)^{LSJ\ \ M_J}_{L'SJ''M_J-1}(s_x-is_y)^{I'S\ J''M_J-1}_{L'S'J\ \ M_J}+l_z{}^{L\ S\ J\ \ M_J}_{L'SJ''M_J}s_z{}^{L'S\ J''M_J}_{L'S'J\ \ M_J}\\ &= (J+1)(2J+3)l^{L\ SJ}_{L'SJ+1}s^{L'S\ J+1}_{L'S'J}+J(J+1)l^{L\ SJ\ \ L'SJ}_{L'SJ}s_{L'S'J}\end{aligned}$$

$$+ J(2J-1)l^{L\,SJ}_{L'SJ-1}s^{L'S\,J-1}_{L'S'J}.$$

Substitution from our previous formulas into the above equation yields the following result for the matrix components of the spin-orbit interaction.

$$(\boldsymbol{l}\cdot\mathbf{s})^{L\;\;S\;\;JM_J}_{L-1S-1JM_J} = -\tfrac{1}{2}(l^{L\;\;S}_{L-1S})(s^{L-1S}_{L-1S-1})\{(L+S-J)(L+S-J-1)(L+S+J)(L+S+J+1)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{L\;\;SJM_J}_{L-1SJM_J} = \tfrac{1}{2}(l^{L\;\;S}_{L-1S})(s^{L-1S}_{L-1S})\{(L+S-J)(J-L+S+1)(J+L-S)(L+S+J+1)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{L\;\;S\;\;JM_J}_{L-1S+1JM_J} = \tfrac{1}{2}(l^{L\;\;S}_{L-1S})(s^{L-1S}_{L-1S+1})\{(J-L+S+2)(J-L+S+1)(J-S+L)(J-S+L-1)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{LS\;\;JM_J}_{LS-1JM_J} = -\tfrac{1}{2}(l^{LS}_{LS})(s^{LS}_{LS-1})\{(L+S-J)(J+L-S+1)(L+S+J+1)(J-L+S)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{LSJM_J}_{LSJM_J} = \tfrac{1}{2}(l^{LS}_{LS})(s^{LS}_{LS})\{J(J+1)-L(L+1)-S(S+1)\}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{LS\;\;JM_J}_{LS+1JM_J} = -\tfrac{1}{2}(l^{LS}_{LS})(s^{LS}_{LS+1})\{(L+S-J+1)(J+L-S)(L+S+J+2)(J-L+S+1)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{L\;\;S\;\;JM_J}_{L+1S-1JM_J} = \tfrac{1}{2}(l^{L\;\;S}_{L+1S})(s^{L+1S}_{L+1S-1})\{(J-L+S)(J-L+S-1)(J+L-S+1)(J+L-S+2)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{L\;\;SJM_J}_{L+1SJM_J} = \tfrac{1}{2}(l^{L\;\;S}_{L+1S})(s^{L+1S}_{L+1S})\{(L+S-J+1)(J-L+S)(J+L-S+1)(L+S+J+2)\}^{1/2}$$

$$(\boldsymbol{l}\cdot\mathbf{s})^{L\;\;S\;\;JM_J}_{L+1S+1JM_J} = -\tfrac{1}{2}(l^{L\;\;S}_{L+1S})(s^{L+1S}_{L+1S+1})\{(L+S-J+1)(L+S-J+2)(L+S+J+2)(L+S+J+3)\}^{1/2}$$

These formulas apply for both electrons. In conjunction with the expressions given above for $l^{LS}_{L'S}$ and $s^{LS}_{LS'}$ they completely determine the matrix of the spin-orbit interaction.

The Configuration p^2

In this case $l_1=l_2=1$ and $a_1=a_2=a$. The multiplets are ^1D, ^3P and ^1S. The energy matrix calculated from the above formulas is given below. It is sufficient to give separate matrices for each J value as there are no components between states of different J value.

$J = 2$

	$^1D_2$	$^3P_2$
$^1D_2$	0	$(\frac{1}{2})^{1/2}a$
$^3P_2$	$(\frac{1}{2})^{1/2}a$	$a/2$

$J = 1$

	$^3P_1$
$^3P_1$	$-a/2$

$J = 0$

	$^3P_0$	$^1S_0$
$^3P_0$	$-a$	$-(2)^{1/2}a$
$^1S_0$	$-(2)^{1/2}a$	0

From Slater's paper we find for the electrostatic energies in terms of his radial integrals

$$^1D: \quad F^0 + 1/25F^2$$
$$^3P: \quad F^0 - 5/25F^2$$
$$^1S: \quad F^0 + 10/25F^2.$$

We now measure energies from the $^3P_1$ level. Then adding the electrostatic energies to the diagonal terms and setting the determinant of the energy matrix equal to zero, we obtain the following secular equations.

$$J = 2 \quad W^2 - W(3/2a + 6/25F^2) + 6/25F^2a = 0$$
$$J = 1 \quad W = 0$$
$$J = 0 \quad W^2 - W(15/25F^2) - 9/4a^2 - 15/50F^2a = 0.$$

These equations determine the energy levels in intermediate coupling in terms of the coupling parameters a and F^2. They have been previously obtained and discussed by Goudsmit.[7]

The Configuration $p \cdot p$

In this case also $l_1 = l_2$ but now $a_1 \neq a_2$. The multiplets are singlet and triplet D, P and S. From our formulas, the energy matrix is

$J = 3$

	$^3D_3$
$^3D_3$	$\frac{1}{2}(a_1 + a_2)$

$J = 2$

	$^3D_2$	$^1D_2$	$^3P_2$
$^3D_2$	$-\frac{1}{4}(a_1 + a_2)$	$-\frac{1}{2}(3/2)^{1/2}(a_1 - a_2)$	$\frac{1}{4}(3)^{1/2}(a_1 - a_2)$
$^1D_2$	$-\frac{1}{2}(3/2)^{1/2}(a_1 - a_2)$	0	$\frac{1}{4}(2)^{1/2}(a_1 + a_2)$
$^3P_2$	$\frac{1}{4}(3)^{1/2}(a_1 - a_2)$	$\frac{1}{4}(2)^{1/2}(a_1 + a_2)$	$\frac{1}{4}(a_1 + a_2)$

$J = 1$

	$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$
$^3D_1$	$-\frac{3}{4}(a_1+a_2)$	$\frac{1}{4}(5/3)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(10/3)^{1/2}(a_1+a_2)$	0
$^3P_1$	$\frac{1}{4}(5/3)^{1/2}(a_1 - a_2)$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	$(\frac{1}{3})^{1/2}(a_1-a_2)$
$^1P_1$	$-\frac{1}{4}(10/3)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	0	$\frac{1}{2}(\frac{2}{3})^{1/2}(a_1+a_2)$
$^3S_1$	0	$(\frac{1}{3})^{1/2}(a_1-a_2)$	$\frac{1}{2}(\frac{2}{3})^{1/2}(a_1 + a_2)$	0

[7] Reference 4. To agree with Goudsmit's results we must set $a/2 = A$ and $3/25\ F^2 = X$ in the above equations.

* In the secular equations the parameters never appear in the denominators of fractions. An expression such as 6/25 F^2 must always be taken to mean (6/25) F^2.

$J=0$		$^3P_0$	$^1S_0$
	$^3P_0$	$-\frac{1}{2}(a_1+a_2)$	$-\frac{1}{2}(2)^{1/2}(a_1-a_2)$
	$^1S_0$	$-\frac{1}{2}(2)^{1/2}(a_1-a_2)$	0

For the electrostatic energies referred to the ^3D multiplet we find by Slater's method[8]

$$
\begin{aligned}
^3D:&\quad 0\\
^1D:&\quad 2G^1+2/25G^2=\alpha\\
^3P:&\quad -6/25F^2+2G^0-4/25G^2=\beta\\
^1P:&\quad -6/25F^2+6/25G^2=\gamma\\
^3S:&\quad 9/25F^2-9/25G^2=-3/2\gamma\\
^1S:&\quad 9/25F^2+2G^0+11/25G^2=\delta.
\end{aligned}
$$

Measuring the energy levels from the $^3D_3$ we obtain the following secular equations

$$
\begin{aligned}
J=3\quad & W=0\\
J=2\quad & -W^3+W^2\{\alpha+\beta-3/2(a_1+a_2)\}-W\{\alpha\beta-\tfrac{1}{4}(a_1+a_2)(4\alpha+5\beta)\\
&+9/4a_1a_2\}-3/4(a_1+a_2)\alpha\beta+\tfrac{3}{4}a_1a_2(\alpha+2\beta)=0\\
J=1\quad & W^4-W^3\{\beta-\tfrac{1}{2}\gamma-3(a_1+a_2)\}+W^2\{-\tfrac{1}{2}\gamma(\beta+3\gamma)\\
&+\tfrac{1}{4}(a_1+a_2)(-9\beta+5\gamma)+9/4(a_1^2+a_2^2+3a_1a_2)\}\\
&-W\{-3/2\beta\gamma^2+\tfrac{1}{8}(a_1+a_2)(7\beta+24\gamma)+3/32(a_1+a_2)^2(12\beta-7\gamma)\\
&-3/32(a_1-a_2^2)\gamma-27/8a_1a_2(a_1+a_2)\}+15/8(a_1+a_2)\beta\gamma^2-5/8(2a_1^2\\
&+29_2^2+5a_1a_2)\gamma^2=0\\
J=0\quad & W^2-W\{\beta+\delta-3/2(a_1+a_2)\}+\beta\delta-\tfrac{1}{2}(a_1+a_2)(\beta+2\delta)+2a_1a_2=0.
\end{aligned}
$$

The Configuration d^2

In this case $l_1=l_2=2$ and $a_1=a_2=a$. The multiplets are ^1G, ^3F, ^1D, ^3P and ^1S. From our formulas the magnetic energy matrix is

$J=4$		$^1G_4$	$^3F_4$
	$^1G_4$	0	a
	$^3F_4$	a	$3/2a$

$J=3$		$^3F_3$
	$^3F_3$	$-\frac{1}{2}a$

$J=2$		$^3F_2$	$^1D_2$	$^3P_2$
	$^3F_2$	$-2a$	$-2(3/5)^{1/2}a$	0
	$^1D_2$	$-2(3/5)^{1/2}a$	0	$(21/10)^{1/2}a$
	$^3P_2$	0	$(21/10)^{1/2}a$	$\frac{1}{2}a$

[8] E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

		$^3P_1$
$J=1$	$^3P_1$	$-\frac{1}{2}a$

		$^3P_0$	$^1S_0$
$J=0$	$^3P_0$	$-a$	$-(6)^{1/2}a$.
	$^1S_0$	$-(6)^{1/2}a$	0

By Slater's method[8] we find for the electrostatic energies referred to the ^3F multiplet

$$^1G: \quad 12/49F^2 + 10/441F^4 = \alpha$$
$$^3F: \quad 0$$
$$^1D: \quad 5/49F^2 + 45/441F^4 = \beta$$
$$^3P: \quad 15/49F^2 - 75/441F^4 = \gamma$$
$$^1S: \quad 22/49F^2 + 135/441F^4 = \delta.$$

Measuring energies from the $^3F_3$ level, we find the following secular equations.

$$J=4 \quad W^2 - W(\alpha + 5/2a) + 2a\alpha = 0$$
$$J=3 \quad -W = 0$$
$$J=2 \quad -W^3 + W^2(\beta+\gamma) - W\{\beta\gamma - \tfrac{1}{2}a(\beta+2\gamma) - 25/4a^2\} - 3/2a\beta\gamma - 3/20a^2(10\beta+21\gamma) = 0$$
$$J=1 \quad -W + \gamma = 0$$
$$J=0 \quad W^2 - W(\gamma+\delta) + \gamma\delta + \tfrac{1}{2}a(\gamma-\delta) - 25/4a^2 = 0.$$

The Configuration $d \cdot d$

In this case $l_1 = l_2 = 2$ but $a_1 \neq a_2$. The multiplets are singlet and triplet S, P, D, F and G. From our formulas the magnetic energy matrix is

		$^3G_5$
$J=5$	$^3G_5$	a_1+a_2

		$^3G_4$	$^1G_4$	$^3F_4$
$J=4$	$^3G_4$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{2}(5)^{1/2}(a_1-a_2)$	$\frac{1}{4}(5)^{1/2}(a_1-a_2)$
	$^1G_4$	$-\frac{1}{2}(5)^{1/2}(a_1-a_2)$	0	$\frac{1}{2}(a_1+a_2)$
	$^3F_4$	$\frac{1}{4}(5)^{1/2}(a_1-a_2)$	$\frac{1}{2}(a_1+a_2)$	$\frac{3}{4}(a_1+a_2)$

		$^3G_3$	$^3F_3$	$^1F_3$	$^3D_3$
$J=3$	$^3G_3$	$-5/4(a_1+a_2)$	$\frac{1}{4}(3/7)^{1/2}(a_1-a_2)$	$-3/2(1/7)^{1/2}(a_1+a_2)$	0
	$^3F_3$	$\frac{3}{4}(3/7)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{2}(3)^{1/2}(a_1-a_2)$	$2(1/7)^{1/2}(a_1-a_2)$
	$^1F_3$	$-3/2(1/7)^{1/2}(a_1+a_2)$	$-\frac{1}{2}(3)^{1/2}(a_1-a_2)$	0	$(3/7)^{1/2}(a_1+a_2)$
	$^3D_3$	0	$2(1/7)^{1/2}(a_1-a_2)$	$(3/7)^{1/2}(a_1+a_2)$	$\frac{1}{2}(a_1+a_2)$

		$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$
$J=2$	$^3F_2$	$-(a_1+a_2)$	$(2/5)^{1/2}(a_1-a_2)$	$-(3/5)^{1/2}(a_1+a_2)$	0
	$^3D_2$	$(2/5)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{4}(6)^{1/2}(a_1-a_2)$	$\frac{3}{4}(7/5)^{1/2}(a_1-a_2)$
	$^1D_2$	$-(3/5)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(6)^{1/2}(a_1-a_2)$	0	$\frac{1}{2}(21/10)^{1/2}(a_1+a_2)$
	$^3P_2$	0	$\frac{3}{4}(7/5)^{1/2}(a_1-a_2)$	$\frac{1}{2}(21/10)^{1/2}(a_1+a_2)$	$\frac{1}{4}(a_1+a_2)$

		$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$
$J=1$	$^3D_1$	$-\frac{3}{4}(a_1+a_2)$	$\frac{1}{4}(7)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(14)^{1/2}(a_1+a_2)$	0
	$^3P_1$	$\frac{1}{4}(7)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	a_1-a_2
	$^1P_1$	$-\frac{1}{4}(14)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(a_1-a_2)$	0	$\frac{1}{2}(2)^{1/2}(a_1+a_2)$
	$^3S_1$	0	a_1-a_2	$\frac{1}{2}(2)^{1/2}(a_1+a_2)$	0

		$^3P_0$	$^1S_0$
$J=0$	$^3P_0$	$-\frac{1}{2}(a_1+a_2)$	$-\frac{1}{2}(6)^{1/2}(a_1+a_2)$
	$^1S_0$	$-\frac{1}{2}(6)^{1/2}(a_1+a_2)$	0

Now we could proceed as before, that is add the electrostatic energies to the diagonal terms of the above matrix and then expand the determinant of the matrix in order to obtain the secular equations. But in this case the expanded fourth order equations are so complicated that it seems preferable to leave them in the form of fourth order determinants, as the determinants are probably easier than the expanded form to handle numerically. For this reason we do not give the expanded form for the secular equations.

The Configuration $d \cdot p$

In this case we have $l_1=2$ and $l_2=1$. The multiplets are singlet and triplet P, D and F. From our formulas the magnetic energy matrix is

		$^3F_4$
$J=4$	$^3F_4$	$\frac{1}{2}(2a_1+a_2)$

		$^3F_3$	$^1F_3$	$^3D_3$
$J=3$	$^3F_3$	$-1/6(2a_1+a_2)$	$-(\frac{1}{3})^{1/2}(2a_1-a_2)$	$\frac{1}{3}(2)^{1/2}(a_1-a_2)$
	$^1F_3$	$-(\frac{1}{3})^{1/2}(2a_1-a_2)$	0	$(1/6)^{1/2}(a_1+a_2)$
	$^3D_3$	$\frac{1}{3}(2)^{1/2}(a_1-a_2)$	$(1/6)^{1/2}(a_1+a_2)$	$1/6(5a_1+a_2)$

		$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$
$J=2$	$^3F_2$	$-\frac{2}{3}(2a_1+a_2)$	$\frac{1}{3}(7/5)^{1/2}(a_1-a_2)$	$-\frac{1}{3}(21/10)^{1/2}(a_1+a_2)$	0
	$^3D_2$	$\frac{1}{3}(7/5)^{1/2}(a_1-a_2)$	$-1/12(5a_1+a_2)$	$-\frac{1}{2}(1/6)^{1/2}(5a_1-a_2)$	$\frac{3}{4}(3/5)^{1/2}(a_1-a_2)$
	$^1D_2$	$-\frac{1}{3}(21/10)^{1/2}(a_1+a_2)$	$-\frac{1}{2}(1/6)^{1/2}(5a_1-a_2)$	0	$\frac{3}{4}(2/5)^{1/2}(a_1+a_2)$
	$^3P_2$	0	$\frac{3}{4}(3/5)^{1/2}(a_1-a_2)$	$\frac{3}{4}(2/5)^{1/2}(a_1+a_2)$	$\frac{1}{4}(3a_1-a_2)$

		$^3D_1$	$^3P_1$	$^1P_1$
$J=1$	$^3D_1$	$-\frac{1}{4}(5a_1+a_2)$	$\frac{1}{4}(3)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(6)^{1/2}(a_1+a_2)$
	$^3P_1$	$\frac{1}{4}(3)^{1/2}(a_1-a_2)$	$-\frac{1}{4}(3a_1-a_2)$	$-\frac{1}{4}(2)^{1/2}(3a_1+a_2)$
	$^1P_1$	$-\frac{1}{4}(6)^{1/2}(a_1+a_2)$	$-\frac{1}{4}(2)^{1/2}(3a_1+a_2)$	0

		$^3P_0$
$J=0$	$^3P_0$	$-\frac{1}{3}(3a_1-a_2)$

.

For the same reason as the previous case we do not give the expanded form of the secular equations.

Many Electron Configurations

Our formulas for four vectors may be applied to give the secular equations relating the levels arising from a common parent term. We take $\boldsymbol{l}_1$ and $\mathbf{s}_1$ for the orbital and spin momentum of the ion and $\boldsymbol{l}_2$ and $\mathbf{s}_2$ for the orbital and spin momentum of the added electron. Then the formulas for the matrix of

the spin-orbit interaction apply directly when we remember that s_1 is no longer restricted to the value 1/2. We must use Eqs. (11) for $s^{LS}_{1LS'}$.

We consider first the addition of an s electron to a ^3P multiplet, a case already treated by Goudsmit.[4] The multiplets are ^4P and ^2P. Remembering that $l_1=l=L$, $s_1=l$, $l_2=0$ and $s_2=1/2$ we have from Eqs. (11)

$$
\begin{aligned}
l^{LS}_{1LS} &= 1 \\
l^{LS}_{2LS} &= 0 \\
s^{LS}_{1LS} &= \frac{S(S+1)+5/4}{2S(S+1)} = \begin{cases} 2/3 \text{ for } {}^4P \\ 4/3 \text{ for } {}^2P \end{cases} \\
s^{LS}_{1LS-1} &= \left(\frac{(25/4-S^2)(S^2-\frac{1}{4})}{4S^2(4S^2-1)}\right)^{1/2}.
\end{aligned}
$$

Our formulas for the matrix of the spin-orbit interaction give

$J = 5/2$

	$^4P_{5/2}$
$^4P_{5/2}$	a_1

$J = 3/2$

	$^4P_{3/2}$	$^2P_{3/2}$
$^4P_{3/2}$	$-\frac{2}{3}a_1$	$-\frac{1}{3}(5)^{1/2}a_1$
$^2P_{3/2}$	$-\frac{1}{3}(5)^{1/2}a_1$	$\frac{2}{3}a_1$

$J = \frac{1}{2}$

	$^4P_{1/2}$	$^2P_{1/2}$
$^4P_{1/2}$	$-5/3a_1$	$-\frac{1}{3}(2)^{1/2}a_1$
$^2P_{1/2}$	$-\frac{1}{3}(2)^{1/2}a_1$	$-\frac{4}{3}a_1$

Let α be the electrostatic energy of the ^2P multiplet referred to the ^4P. Then measuring energies from the $^4P_{5/2}$ level we obtain the following secular equations

$$
\begin{aligned}
J = 5/2 \qquad & -W = 0 \\
J = 3/2 \qquad & W^2 - (\alpha - 2a_1)W - 5/3\alpha a_1 = 0 \\
J = \tfrac{1}{2} \qquad & W^2 - (\alpha - 5a_1)W - 8/3\alpha a_1 + 6a_1^2 = 0.
\end{aligned}
$$

As another example we consider the addition of a p electron to a ^1P multiplet. The multiplets are ^2S, ^2P and ^2D. From Eqs. (11), remembering that $l_1=1$, $s_1=0$, $l_2=1$, $s_2=1/2=S$, we have

$$
\begin{aligned}
s^{LS}_{1LS} &= 0 \\
s^{LS}_{2LS} &= 1 \\
l^{LS}_{2LS} &= \tfrac{1}{2} \\
l^{L\ S}_{2L-1S} &= \tfrac{1}{2}\left(\frac{9-L^2}{4L^2-1}\right)^{1/2}.
\end{aligned}
$$

Then we find for the matrix of the spin-orbit interaction

$J = 5/2$

	$^2D_{5/2}$
$^2D_{5/2}$	$\frac{1}{2}a_2$

$J = 3/2$

	$^2D_{3/2}$	$^2P_{3/2}$
$^2D_{3/2}$	$-\frac{3}{4}a_2$	$\frac{1}{4}(5)^{1/2}a_2$
$^2P_{3/2}$	$\frac{1}{4}(5)^{1/2}a_2$	$\frac{1}{4}a_2$

$J = \frac{1}{2}$

	$^2P_{1/2}$	$^2S_{1/2}$
$^2P_{1/2}$	$-\frac{1}{2}a_2$	$\frac{1}{2}(2/5)^{1/2}a_2$
$^2S_{1/2}$	$\frac{1}{2}(2/5)^{1/2}a_2$	0

.

Let α be the electrostatic energy of the ^2P multiplet referred to the ^2D and β be the electrostatic energy of the ^2S referred to the ^2D. Measuring energies from the $^2D_{5/2}$ level we obtain the following secular equations.

$J = 5/2 \qquad -W = 0$

$J = 3/2 \qquad W^2 - (\alpha - 2a_2)W + 5/8a_2(a_2 - 2\alpha) = 0$

$J = \frac{1}{2} \qquad W^2 - (\alpha + \beta - 3/2a_2)W + \alpha\beta - \frac{1}{2}a_2(\alpha + 2\beta) + 2/5a_2^2 = 0$

The Adjustment of the Parameters

In the secular equations that we have given the coefficients are functions of the radial integrals F^k, G^k and a_1 and a_2. Until these integrals can be calculated they must be treated as parameters which may be adjusted to fit the experimental data. In simple cases this may be accomplished easily by using the sums of energies for each J value. These sums are always linear in the parameters so that if we set the various sums equal to their experimental values, we obtain a linear set of equations for the parameters. In more complicated cases we will not obtain enough equations to determine the parameters in this way and more laborious calculations will have to be made. However these calculations will be useful for other quantities besides the energy levels may be found in terms of the same parameters. Thus in the following paper the g values for intermediate coupling are calculated in terms of these parameters and in a later paper the writer will treat the question of intensities in intermediate coupling.

In conclusion the writer wishes to thank Professor Pauli for suggesting the method of treating this problem.

ZEEMAN EFFECT IN INTERMEDIATE COUPLING

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Abstract

A method is given for calculating g-values in intermediate coupling when the matrix of internal energy of the atom (spin-orbit plus electrostatic interaction) is known in LS coupling. The transformation from the states of LS coupling to the states of intermediate coupling, in which the internal energy matrix is diagonal, is then readily determined in terms of the parameters expressing the relative magnitudes of the interactions. The coupling parameters are ascertained from the measured energy levels. The transformation so determined is applied to the matrix of the energy due to an external magnetic field, as known for LS coupling. The diagonal terms of the transformed matrix contain the g-values of the states of the atom in intermediate coupling. Application of the method is made to the configurations p^2, p^3 and d^2. Agreement with the available experimental g-values is satisfactory, being as good as the agreement of energy levels to be had from a first order calculation.

THE "anomalous" Zeeman effect for two-electron configurations with one s-electron has been treated by Houston.[1] Goudsmit[2] has extended the treatment to another special type of configuration, p^2 and p^4. The energy level problem for general two-electron configurations has been treated in the preceding paper in a manner which makes possible an easy method for calculating g-values in intermediate coupling. The method applies to any atom of which the matrix of the perturbing energy of the electrons is known in LS coupling.

Zeeman effect (as distinguished from Paschen-Back effect) is concerned with an external magnetic field sufficiently weak that the magnitude of the total angular momentum is a constant of the motion. Then the components of the energy matrix between states of different values of J may be neglected. In LS coupling L^2, S^2 and J_z are diagonal matrices (being constants of the motion), and they commute with L_z and S_z. Thus the energy due to the external field, $(L_z+2S_z)H$, has matrix elements only between states with the same quantum numbers L, S and M_J. As we neglect the elements between states of different J value, this Zeeman energy is a diagonal matrix in LS coupling. From Eqs. (3), (4) and (5) of the preceding paper, we have the familiar result

$$\begin{aligned} H(L_z + 2S_z)^{LSJM_J}_{LSJM_J} &= HM_J(L^{LSJ}_{LSJ} + 2S^{LSJ}_{LSJ}) \\ &= HM_J \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \\ &= HM_J g_{LSJ} \end{aligned} \tag{1}$$

giving the Landé g-values in LS coupling.

[1] W. V. Houston, Phys. Rev. **33**, 297 (1929).
[2] S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

If we know the matrix of the internal energy of the atom in LS coupling, we can find the transformation, R, which carries it to diagonal form. R will have no components between states of different J and M_J, as the internal energy commutes with J^2 and J_z. Hence it is sufficient to consider together states with the same J and M_J.

The matrix of the energy due to the external field is diagonal in LS coupling, and has the elements HM_Jg_k, where g_k is the g-value of a state specified by the quantum numbers $L_kS_kJ_k$. This matrix may be transformed to intermediate coupling:

$$HM_Jg' = HM_JRgR^{-1}.$$

We treat the energy due to the external field as a perturbation of the atom in intermediate coupling, expanding in powers of the perturbation parameter H. The first order corrections to the energies are the diagonal elements of the perturbing energy matrix. The g-values are defined by the coefficients of the first power of H in the energies,[3] so they are the diagonal terms

$$g_k' = \sum_l R(kl)g_lR^{-1}(lk) = \sum_l R(kl)g_lR^*(kl). \tag{2}$$

Applications

The configuration p^2. Here the levels with $J=0$ are not split up by the field and the level with $J=1$, $^3P_1$, has $g=3/2$ for all couplings. For the levels with $J=2$ the matrix of the g-values in LS coupling is

	$^1D_2$	$^3P_2$
$^1D_2$	1	0
$^3P_2$	0	3/2

Using the energy matrix from the preceding paper (with $^3P_1$ as reference level), we find for the transformation matrix,

$$R(k1) = \frac{2^{1/2}(\epsilon_k - 1)}{[2(\epsilon_k - 1)^2 + 1]^{1/2}}$$

$$R(k2) = \frac{1}{[2(\epsilon_k - 1)^2 + 1]^{1/2}}.$$

In these equations $\epsilon_k = W_k/a$, where W_k is the energy of a state in intermediate coupling (a solution of the secular equation for $J=2$ in the preceding paper) and a is the parameter of spin-orbit interaction. We find for the g-values in intermediate coupling[4]

[3] The g-values are thus independent of the nondiagonal elements of the transformed matrix, and therefore small elements of the matrix that are nondiagonal with respect to J^2 in LS coupling do not affect the g-values.

[4] With Goudsmit's method,[2] which applies especially to this case, we obtain the formula

$$g_k' = \frac{5}{4} + \frac{1/4 - X/a}{2(\epsilon_k - \epsilon_e)}$$

$$g_k' = \frac{2(\epsilon_k - 1)^2 + 3/2}{2(\epsilon_k - 1)^2 + 1}.$$

This formula has been applied in calculating the values listed in Table I. The parameters have been determined simply from their relations to the energy

TABLE I. *Energies and g-values of the configuration p^2.*

	Sn I $5p^2$					Pb I $6p^2$				
	$J=0$	2	2	1	0	$J=0$	2	2	1	0
ν obs.	15471	6921	1736	0	−1692	21639	13639	2831	0	−7817
ϵ_k obs.	7.39	3.31	0.83	0	−0.81	2.96	1.87	0.39	0	−1.07
ϵ_k calc.	7.34	3.35	0.78	0	−0.76	2.97	1.85	0.41	0	−1.08
g (LS)		1.00	1.50	1.50			1.00	1.50	1.50	
g_k' calc.		1.042	1.458	1.50			1.205	1.295	1.50	
g_k' obs.*		1.050	1.420	1.501			1.230	1.269	1.501	

* E. Back, Zeits. f. Physik **43,** 309 (1927). The g-values for Sn I observed by Green and Loring (Phys. Rev. **30,** 574, 1927) agree with Back's, except that they have 1.46 instead of 1.420, in better agreement with the theoretical value and with the g-sum rule.

sums. The energy values calculated from these parameters are also listed, and are seen to agree with the observed levels as well as is to be expected from a first order calculation.

The configuration p^3. For this case the multiplets are ^2D, ^2P, and ^4S. The g-values for $^2D_{5/2}$ and $^2P_{1/2}$ are independent of the coupling. For the levels with $J=3/2$ the equation for the energies has been given by one of us[5] as

$$W^3 + W^2X - W(9a^2/4 + 6X^2) - 15Xa^2/4 = 0.$$

The energies of the states in LS coupling are known, and contain no term in the first power of a. This and the selection rule that $\Delta L = 0, \pm 1$ and $\Delta S = 0, \pm 1$ for the matrix components of the spin-orbit interaction limit the energy matrix to the form

	$^2D_{3/2}$	$^2P_{3/2}$	$^4S_{3/2}$
$^2D_{3/2}$	0	α_1	0
$^2P_{3/2}$	α_1	$2X$	α_2
$^4S_{3/2}$	0	α_2	$-3X$

with $^2D_{5/2}$ taken as reference level. This yields the secular equation

$$W^3 + W^2X - W(\alpha_1^2 + \alpha_2^2 + 6X^2) - 3X\alpha_1^2 = 0.$$

(his equation 13). Application of this formula also gives the results of Table I. It differs from ours in form, since his method is a solution of a secular equation directly for energies, and involves no transformation coefficients. It is equivalent to solving the equation

$$\begin{vmatrix} e_{11} + g_1 H - \epsilon_0 - g'H & e_{12} \\ e_{21} & e_{22} + g_0 H - \epsilon_0 - g'H \end{vmatrix} = 0$$

where the terms without H vanish, ϵ_0 being a solution for zero field. When we go to determinants of higher order, the coefficient of H involves nondiagonal elements. A direct solution of the determinant becomes increasingly unwieldy, and Goudsmit's method fails with too few relations to determine the coefficients.

[5] D. R. Inglis, Phys. Rev. **38,** 377 (1931).

Comparison with the above determines[6]

$$\alpha_1^2 = 5a^2/4$$
$$\alpha_2^2 = a^2$$

For the transformation matrix we find

$$R(k1) = \frac{5^{1/2}}{2}\,\frac{\epsilon_k + 3X/a}{\epsilon_k}\,R(k3)$$
$$R(k2) = (\epsilon_k + 3X/a)R(k3)$$
$$R(k3) = \frac{1}{[1 + (5/4\epsilon_k + 1)(\epsilon_k + 3X/a)]^{1/2}}.$$

In LS coupling

$$g = \begin{array}{c|ccc} & {}^2D_{3/2} & {}^2P_{3/2} & {}^4S_{3/2} \\ \hline {}^2D_{3/2} & 4/5 & 0 & 0 \\ {}^2P_{3/2} & 0 & 4/3 & 0 \\ {}^4S_{3/2} & 0 & 0 & 2 \end{array}$$

Hence for the g-values in intermediate coupling we have

$$g_k' = \frac{\epsilon_k^2 + (4\epsilon_k^2/3 + 1)(\epsilon_k + 3X/a)}{\epsilon_k^2 + (\epsilon_k^2 + 5)(\epsilon_k + 3X/a)}.$$

The comparison with experimental data[7] is indicated in Table II.

TABLE II. *Energies and g-values of Bi I, $6p^3$.*

	$J=1\frac{1}{2}$	$\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$
ν obs.	17728	6223	0	−4018	−15437
ϵ_k obs.	1.81	0.637	0	−0.41	−1.58
ϵ_k calc.[5]	1.73	0.637	0	−0.44	−1.62
g (LS)	4/3	2/3	6/5	4/5	2
g_k' calc.	1.25			1.25	1.66
g_k' obs.	(1.26)			1.225	1.65*

* A tentative value kindly communicated to us by R. F. Bacher. The other measured value is taken from his dissertation (Michigan, 1930). The value in parentheses is known only from the measurements of the others through the sum rule.

The configuration d^2. In this case the levels with $J=4$ and with $J=2$ are of interest. For the levels with $J=4$, we find the following transformation matrix when the energy matrix of the preceding paper is used and ${}^3F_3$ is taken as reference level:

[6] A similar determination is possible in other very simple cases where we know the secular equation from consideration of extreme couplings. In these few cases we are not dependent upon the preceding paper, or the method of Gray and Wills, for the energy matrix.

[7] The only further measurements of "anomalous" g-values for interesting configurations of which we are aware are for Ne I, $2p^53p$. Here the magnetic parameters may be estimated from the doublet separations of Ne II and Na I, but we have found no satisfactory fit for the energies, so no g-values could be calculated.

$$R(k1) = \frac{\epsilon_k - 2}{[(\epsilon_k - 2)^2 + 1]^{1/2}} \qquad R(k2) = \frac{1}{[(\epsilon_k - 2)^2 + 1]^{1/2}}$$

In LS coupling we have

$$g = \begin{array}{c|cc} & {}^1G_4 & {}^3F_4 \\ \hline {}^1G_4 & 1 & 0 \\ {}^3F_4 & 0 & 5/4 \end{array}$$

Then, in intermediate coupling,

$$g_k' = \frac{(\epsilon_k - 2)^2 + 5/4}{(\epsilon_k - 2)^2 + 1}.$$

For the levels with $J=2$ the transformation coefficients are

$$R(k1) = -\frac{2(3/5)^{1/2}}{\epsilon_k + 3/2} R(k2)$$

$$R(k2) = \left[\frac{12}{5(\epsilon_k + 3/2)^2} + \frac{21}{10(\epsilon_k - \gamma/a - 1)^2} + 1\right]^{-1/2}$$

$$R(k3) = \frac{(21/10)^{1/2}}{\epsilon_k - \gamma/a - 1} R(k2)$$

where $\gamma = (15/49)F^2 - (75/441)F^4$. From the matrix

$$g = \begin{array}{c|ccc} & {}^3F_2 & {}^1D_2 & {}^3P_2 \\ \hline {}^3F_2 & 2/3 & 0 & 0 \\ {}^1D_2 & 0 & 1 & 0 \\ {}^3P_2 & 0 & 0 & 3/2 \end{array}$$

we get the g-values in intermediate coupling,

$$g_k' = \frac{\{32 + 20(\epsilon_k + 3/2)^2\}(\epsilon_k - \gamma/a - 1)^2 + 63(\epsilon_k + 3/2)^2}{\{48 + 20(\epsilon_k + 3/2)^2\}(\epsilon_k - \gamma/a - 1)^2 + 42(\epsilon_k + 3/2)^2}.$$

Conclusion

The agreement of calculated Zeeman effect with experiment, judged by percentage discrepancy, is usually[8] considerably better than the agreement of observed and calculated energy levels, after adjustment of the radial-integral parameters. In judging calculations of g-values, however, one must bear in mind that they vary between quite narrow limits while the parameters of energy vary all the way from the parameters of LS to those of (jj) coupling. A fairer criterion of agreement of an intermediate-coupling g-value is then the relative error in the deviation from the extreme-coupling g-value. One cannot expect greater accuracy in the calculation of g-values than in the

[8] See also reference 1; Laporte and Inglis, Phys. Rev. **35**, 1337 (1930); J. Bakker, Naturwiss., **18**, 1100 (1930).

calculation of energy separations in a first-order treatment of this sort. A disagreement of energy levels with theoretical values causes a maladjustment of parameters, which makes an error in the g-value calculated in terms of the parameters. In addition, there are errors due to second-order contributions of the states of other configurations to the g-values directly. In Tables I and II, the agreement of the g-values with experiment is entirely satisfactory.

Application of the method has here been made to only a few of the simplest cases.[9] Calculation of g-values of other two-electron configurations should be of interest with extension of the experimental data. For more than two electrons, the calculations are also possible, but are limited by the difficulty in determining the energy matrix for configurations in which the same multiplet appears more than once.

[9] *Footnote added in proof, October 14*: Calculations for p^2 by the method of Goudsmit, corresponding to and agreeing with Table I, are given by Green and Loring (Phys. Rev. in print). In the preparation of Table II, the magnetic data for Sb I (H. Löwenthal, Zeits. f. Physik **57,** 828 (1929); Green and Loring, Phys. Rev. **31,** 707 (1928) were overlooked. They agree satisfactorily with the theory:

TABLE II, *A*. *g-values of Sb I, $5p^3$.*

J	$1\frac{1}{2}$	$\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$
ϵ_k obs.	2.72	1.86	0	−0.38	−2.79
ϵ_k calc.	2.51	1.86	0	−0.46	−3.02
g_k calc.	1.267	2/3	6/5	0.908	1.955
g_k obs.	1.280	0.668	1.205	0.898	1.967

For this configuration, $a=3520$, $X=3270$. For As I, $4p^3$, which is near (LS) coupling, the predicted g-values are 1.319, 2/3, 6/5, 0.825, and 1.988.

It has been remarked (Green and Loring, Phys. Rev. in print; L. A. Young, W. V. Houston, in conversation) that much of the disagreement between theoretical and experimental energy levels may be due to our neglect in the Hamiltonian of those terms corresponding to coupling of the spin of one electron to the orbit of the other, and to spin-spin interaction, which assume importance in the triplets of He and Li^+. These neglected terms become relatively small linearly with increasing *effective* nuclear charge. They are thus expected to be smaller for the configurations p^5s and d^9s than for ps, ds, p^5p, etc. It has been apparent (reference 8) that the agreement is indeed more satisfactory in the former cases, provided there be no overlapping of configurations.

ABSORPTION SPECTRA OF SALTS IN LIQUID AMMONIA

By R. W. Wood
Johns Hopkins University
(Received September 21, 1931)

Abstract

A preliminary investigation of the modifications in appearance and position of absorption bands of colored metallic salts and organic compounds dissolved in anhydrous liquid ammonia.

THE absorption spectra of solutions of metallic salts, having narrow absorption bands, in anhydrous liquid ammonia have not been studied so far as I have been able to discover.

The bands are modified in a very striking manner, due chiefly, I believe, to the nature of the solvent rather than to its low temperature, which is only −38 degrees, scarcely low enough to account for the observed changes.

The first experiments were made with solutions of salts of the rare earths, not all of which were soluble, however. The most striking results were ob-

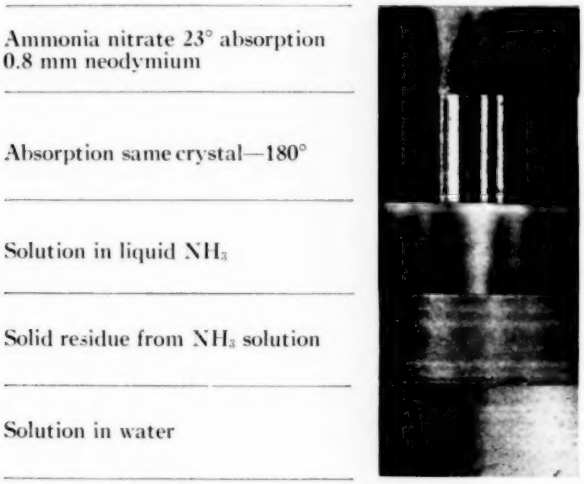

Fig. 1. The absorption band in the yellow.

tained with neodymium ammonium nitrate, the rather broad double bands in the yellow, shown by water solutions, breaking up in five rather narrow and completely separated bands. The ammonia was drawn from an inverted iron tank directly into a Dewar flask, the operation being performed in the open air, of course. The liquid can then be handled in the same way as liquid air. Incidentally, it may be mentioned that the liquid forms a convenient constant low temperature bath.

The solutions were contained in a small cylindrical Dewar flask of fused quartz placed in front of the slit of the spectrograph, at such a distance as to focus the source on the slit.

The absorption band in the yellow is shown in its various modifications in Fig. 1, reproduced as a negative, i.e., the dark absorption bands are shown white. The upper spectrum is that of a crystal of the double salt, 0.8 mm in thickness at room temperature. The next below that of the same crystal at −180 degrees, the crystal in this case being mounted just above the surface of liquid air, which was boiling quietly in the Dewar flask. Here we find ex-

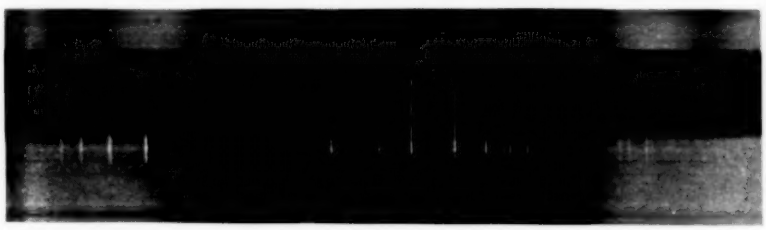

Fig. 2.

tremely narrow absorption lines. Below this is the absorption of a solution of the salt in liquid ammonia, a group of five rather narrow bands well separated but much expanded.

On evaporation the ammonia solution deposits a glassy crust on the floor of the Dewar flask, this substance being insoluble both in ammonia and in water. This seems to be a somewhat unique case, a solid residue by evapora-

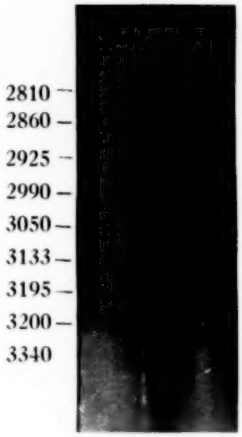

Fig. 3.

tion, which is insoluble in the solvent. I have not yet tried evaporation in vacuo or in a hydrogen atmosphere, which I suppose is the next logical proceeding to see whether a chemical change has resulted from contact with the air. The absorption spectrum of this solid residue is shown below that of the ammonia solution.

Below this is given the spectrum of a water solution, the band being very broad and shifted towards the red. All five spectra are in exact coincidence. Potassium permanganate dissolves readily in ammonia giving a purple solu-

tion similar in color to the water solution. The absorption bands in the green are, however, much less diffuse, and the contrast between the bright and dark regions of the spectrum is much greater than in the case of an aqueous solution. The upper spectrum of Fig. 2 is that of the ammonia solution, the lower that of a solution in water, the iron spectrum dividing the two for comparison.

A previously unrecorded set of bands was found in the ultraviolet, but they appear only with a very dilute solution, showing a bare trace of purple color by transmitted light. These bands are shown in Fig. 3, with their wave-lengths indicated. Continuous absorption is given for this region in all references that have come to my knowledge. I have observed a very faint trace of them in photographs made of a dilute water solution, though I doubt if I should have noticed them, if their presence had not been indicated by the ammonia solution. Both photographs are reproduced as positives, the absorption bands being dark. The wave-lengths of the ultraviolet bands were determined from the very narrow spectrum of the cadmium spark superposed on the absorption spectrum.

Many aniline dyes, and other fluorescent and nonfluorescent compounds are soluble in liquid ammonia, the absorption bands being modified in an analogous manner, and it appears probable that useful filters for suppressing certain spectrum regions may result from a further investigation of these solutions. The work is to be continued.

THE APPEARANCES OF THE FORBIDDEN LINES AND THE INTENSITY MODIFICATIONS OF THE SPECTRA OF MERCURY, CADMIUM AND ZINC UNDER HIGH FREQUENCY EXCITATION

By J. Okubo and E. Matuyama
Tohuku Imperial University

(Received July 27, 1931)

Abstract

With an oscillator of frequency 3×10^7 cycles per sec. the intensity modifications of the spectra of mercury, cadmium and zinc were studied. The singlet series and the intercombination lines which begin on the singlet levels were strengthened as has been observed by previous investigators in the case of mercury and the results were extended to the case of cadmium and zinc. Further, the intensity relations of the forbidden line $1S-2p_1$ of mercury were studied under this condition of excitation and also $1S-2p_{1,3}$ of cadmium were observed. The relations between the lines and the bands are discussed. Some consideration is also given to the conditions of excitation from the intensity modifications of lines.

IN RECENT years, many experimenters have drawn attention to the luminous phenomena produced in gases at very low pressures by a high frequency electrical oscillation with comparatively low potentials. Many efforts have been made to investigate the exciting and the ionizing processes of gases under these circumstances. However many unsolved questions still remain. The results of the spectroscopic observations of mercury show that the intensities of the lines show remarkable differences compared with those in the arc. The results generally may be summarized as follows; all the singlet series and the lines which begin on the singlet levels are strengthened while the triplet series and the lines which begin on the triplet levels are weakened or remain unaltered. Obviously, under these circumstances, the atoms or molecules are excited or ionized under conditions noticeably different from those in the usual arcs, or in Geissler tubes and it is very desirable to study this more fully and to extend the spectroscopic observations to other gases and vapors.

The present paper is a report of some experimental work in this field extending it to the vapors of cadmium and zinc as well. It also describes the appearance of forbidden lines in addition to the intensity modifications of the series lines that were observed.

The arrangement of the apparatus used, as is shown in Fig. 1, is quite similar to that used by S. Tolansky[1] in his investigation of mercury. The discharge tube was made of transparent fused silica 15 cm long with a 2 cm bore around which were wrapped two thin strips of tin, 2 cm wide, that served as electrodes which connected it with a secondary circuit coupled with

[1] S. Tolansky, Proc. Phys. Soc. **A42**, 556 (1930).

Lecher wires of a 10 meter oscillator arranged after the manner of E. W. Gill and R. H. Donaldson. The discharge is brightest for a given length of the secondary circuit, and the light from this tube was observed always in an end-on view. The plate voltages applied to the valve were from 300 up to 600 volts while the plate current was about 20 m.a. The vapors were evaporated from the metals placed in the middle of the tube, which was coaxially heated by a cylindrical electric resistance furnace 30 cm long and 9 cm in diameter.

Experimental Results

1. Mercury. Since the first observation of J. R. Clark,[2] and M. Ponte* many investigations of the intensity modifications of the spectra in mercury have been carried out. Recently S. Tolansky,[1] using an electrodeless discharge and extending the region of observations from λ7000A to λ2400A, obtained the general results on the intensity modifications already referred to. He also examined the fine structures of lines λ5461A and λ4916A.

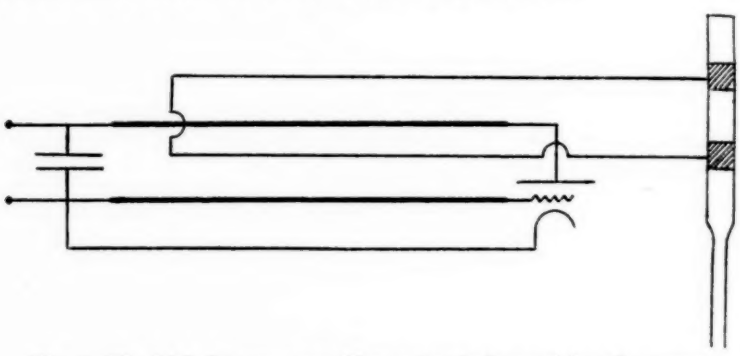

Fig. 1. The high frequency oscillator circuit for exciting the vapors.

In the present experiment, the spectra were photographed in the region from λ7000A to λ2000A. The observations of Tolansky on the strengthening and the weakening of the singlet and the triplet lines are confirmed and in addition it was observed that the forbidden line $1S-2p_1$ is emitted in this discharge and also that the intensities of some unclassified lines are markedly reduced with rise of temperature.

The forbidden line $1S-2p_1$ is observed weakly in the spectra emitted from the vapor at room temperature. Heating the tube caused the discharge to become brighter and the line $1S-2p_1$ was much more strengthened than the neighboring diffuse triplet lines $2p_2-12d$ and $2p_2-13d$ as is shown in Figs. 2a and 2b which are reproductions of the photometric curves of spectra emitted from the vapor at 70°C and at the room temperature respectively. From the figure, it is also observable that the vapor at 70°C is able to emit only lines classified in the sharp and the diffuse triplet series with remarkable regularities of intensities while there are found, at room temperature, some spark lines λλ2224A, 2260A, and 2262A in addition to the triplet lines with an irregular distribution of intensities. It is very interesting that a change of tem-

[2] J. R. Clark, Nature **120**, 727 (1927).
* M. Ponte, Nature **121**, 243 (1928).

perature of some fifty degrees has such a considerable influence on the intensities of the lines.

T. Takamine[3] has already, in the case of the so-called branched arc, investigated the dependence of the intensities of the forbidden line $1S-2p_1$, and

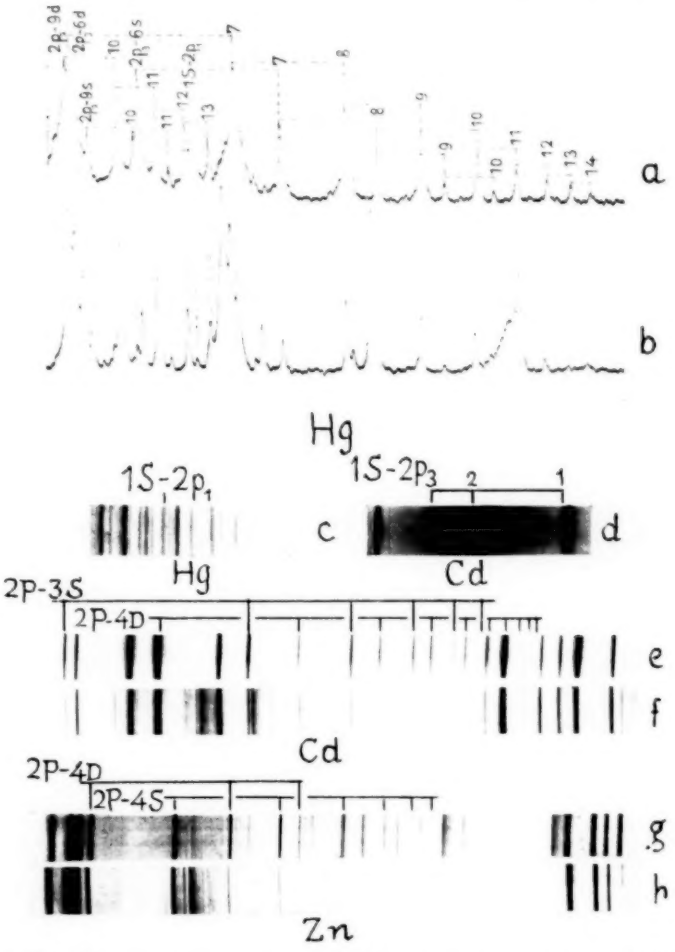

Fig. 2. (a) The photometric curve of the forbidden line $1S$-$2p_1$ and its neighbouring lines of mercury at 70°C. (b) The same, at room temperature (at about 20°C). (c) The spectra of mercury, the photometric curve of which has shown in (a). (d) The appearances of the forbidden lines of cadmium ($2p_3$ was missed in the reproducing process). (e) The spectra of cadmium showing the development of higher members of the singlet series under the high frequency excitation. (f) The spectra in the same region in a vacuum arc with a hot cathode. (g) The spectra of zinc showing the developments of higher members of the singlet series under the high frequency excitation. (h) The spectra in the same region in a vacuum arc with a hot cathode.

the neighboring classified and unclassified lines on the current density. He found that, except in observations at the part near the main arc, the forbidden line is strengthened very rapidly at first and, after attaining a maximum, decreases again slowly with increase of the current density. All other neigh-

[3] T. Takamine, Zeits. f. Physik **37,** 72 (1926).

boring lines gradually are enhanced with the current density. With this observation on the branched arc in mind, the enhancement of the forbidden line in the case given in Fig. 2a may be accounted for as being due to the increase of the current density with rise of temperature. However, as the vapors are, in both cases, under quite different conditions of excitation, the spectra emitted are not similar and therefore it will be adequate to seek for other reasons that the forbidden lines in this experimental condition are much more strengthened than other neighboring lines. Probably the main causes are the increase in number of low speed electrons and in the frequency of collisions between atoms and electrons resulting from the increase of pressure.

It is very interesting to observe that the band at 2345A is lacking in the spectra in the high frequency excitations, in spite of the fact that it is strongly emitted in the branched and the distilled arcs. T. Takamine[3] has already found that the band enhances hand in hand with the forbidden line and has suggested that the conditions favorable to exciting the forbidden line are also the conditions favorable to forming the molecules emitting the band at 2345A. However, in the high frequency excitation, it was found that the forbidden line was observable independent of the band and it seems that there are, at least in this case of excitation, no intimate connections between the line and the band. On the contrary the band at 2482A seems to have some relation with the forbidden line, as only this band has appeared strongly in the vapor at about 70°C at which the line enhances, while it disappeared at room temperature.

This band has been explained by Condon as the nuclear diffraction band, and suggested that it is emitted by the Hg_2 molecules excited in the initial state from which the molecule separates into the normal and the metastable p_1 atoms. The above mentioned relations between the band and the forbidden line seem to favor his suggestion regarding the initial level of the band.

2. **Cadmium.** The vapor was evaporated from Kahlbaum cadmium placed in the tube which was heated coaxially with a cylindrical electric furnace. The pressure of the vapor was estimated as about 0.05 mm Hg.

Careful examination of the spectra obtained showed that the singlet series especially the singlet diffuse series, are strengthened and were observed with moderate exposures up to the line $1P-12D$.

In consequence of the fact that atoms excited in D-levels are strongly concentrated, the intercombination lines which begin on D-levels are also strengthened and 7 members in the p-D combination are easily observed. The p-S combination lines are also strengthened as are the P-D combinations. Similar to the observations of Tolansky in mercury, the intercombination lines beginning on the triplet levels undergo generally slight intensity modifications.

It is worthy of notice that four intense lines of pp' combinations in the arc are lacking in this case of excitation. As the lines, according to the classification of R. A. Sawyer,[4] begin on the triplet levels, the intensity reductions

[4] R. A. Sawyer, Jour. Opt. Soc. Amer. **13**, 431 (1926).

will be due to the decreasing of the number of atoms excited to the initial levels.

The forbidden lines $1S$–$2P_1$ and $1S$–$2p_3$ were clearly observed as in the case of mercury and they are reproduced in Fig. 2d.

3. **Zinc.** Similar observations were made on the vapor of zinc. Just as in the case of the former two metals, the singlet series, especially the singlet sharp series lines enhanced while triplet lines remained unaltered. Ten members of the singlet sharp series and 4 members of the singlet diffuse series were observed. The intercombination lines were not so well excited as in the case of cadmium and the resonance line was markedly strengthened.

It is also to be regretted that the forbidden lines were not found in this case.

Under the conditions involved in high frequency discharges, the vapors are excited at very low pressures with comparatively low voltages and it is to be expected that the spectra of comparatively high potentials will be emitted because of the increase of mean free path of electrons. The excitation functions of spectral lines has been studied by R. Seeliger and his coworkers and recently more carefully and quantitatively by W. Hanle.[5,6] He has shown that, in the cases of helium, neon and mercury, the maximum of the excitation functions of triplet lines are sharp while those of singlet lines are flat and lie about thirty or more volts higher than the former. Considering that the electrons having velocities corresponding to about twenty volts predominate in this discharge and that the excitation functions of the lines are determinable with the initial levels, the strengthening of the singlet lines and of the intercombination lines beginning on the singlet levels and the reductions of the triplet lines and the intercombination lines which begin on the triplet levels are well accounted for.

In the branched arcs, the forbidden lines vanish when the current density through the tube is increased to the point at which the *p-d* lines show sensible broadening. Since the vapors in this experimental condition are at very low pressures and the current density is small, the interatomic field will certainly be very weak and this will also be one of the favorable conditions for the appearance of the forbidden lines. It is also true that a slight rise of temperature in the case of mercury brings the vapor to a more favorable condition as the result of the increase in pressure and in the numbers of electrons.

The assumption that the atoms are, in the high frequency discharge, more uniformly excited with electrons having higher velocities than in the case of arcs, accounts for the intensity modifications of spectra in this discharge. In the cases of mercury and helium we have many detailed studies by many authors on the excitation function and the influence of pressure on the spectral intensity. From this point of view further photometric studies of the spectra of mercury and helium under this excitation condition will be very interesting. The experiment is now in progress and will be reported on another occasion.

[5] W. Hanle, Zeits. f. Physik **56**, 94 (1929).
[6] W. Hanle, Phys. Zeits. **30**, 902 (1929).

DIFFUSION OF ELECTRONS BACK TO AN EMITTING ELECTRODE IN A GAS

By Irving Langmuir
General Electric Company, Schenectady, N. Y.
(Received September 23, 1931)

Abstract

An expression is derived for the current i between two electrodes, one of which emits (with uniform current density I_0) electrons with an initial volt velocity, V_0, when the electrodes are placed in a gas at such a pressure that the electrons suffer only elastic collisions. If V is the voltage between the electrodes, λ the mean free path of an electron, the current is given by

$$i = (16\pi/3)I_0\lambda C\phi$$

where C is the electrostatic capacitance between the electrodes and

$$\phi = (V/V_0)\ln(1 + V/V_0).$$

If the emitted electrons have a Maxwellian velocity distribution, this equation is applicable with slightly modified values of ϕ, V_0 now being replaced by $T/11600$ volts.

IN SOME recent investigations[1] it was observed that the electron current from a negatively charged electron-emitting electrode in neon at 1 mm pressure did not reach a saturation value, but continued to increase with increasing applied potential, although the currents were so small that space charge effects could be neglected. The conditions of the experiment were such that the electrons, which were probably emitted with a uniform initial velocity, suffered elastic collisions with gas atoms, and the mean free path was so short that the energy gained from the field between collisions was small compared to the initial velocity of electrons. It was thought that under these conditions, electrons leaving the electrode would, as a result of the elastic collisions, diffuse back to the cathode. The following paper contains the derivation of an expression for the current from an electron-emitting electrode as a function of voltage under these conditions.

The motion of slow electrons moving in a gas under the influence of an electric field has been considered theoretically by Hertz[2] for conditions similar to those stated above except that the electrons were assumed to have zero initial velocity. In these investigations he obtained the following expression for the drift velocity of an electron

$$v_x = \frac{1}{3}\frac{\gamma\lambda}{v} - \frac{v\lambda}{3}\frac{1}{n}\cdot\frac{dn}{dx} \tag{1}$$

where v is the velocity of an electron along its path; v_x the drift velocity of an electron in direction of the field; $\gamma = (e/m)(dV/dx)$ is the acceleration of an electron in the direction of the electric field; and λ is the electronic mean free

[1] See a recent letter to the editor. I. Langmuir and C. G. Found, Phys. Rev. **36**, 604 (1930).
[2] Hertz, Zeits. f. Physik **32**, 278 (1925).

path. In this equation the 2nd term in the right member represents the effect of diffusion, the diffusion coefficient D being

$$D = (\tfrac{1}{3})v\lambda.$$

If the electron velocities were everywhere uniform throughout the gas as has often previously been assumed in considering the mobility of electrons, the effect of the field would be to cause a drift with velocity $v_x = \gamma\lambda/v$.

The 1st term in the right member of Eq. (1), however, is only 1/3 as great as this expression for the mobility. This is due to the fact that in Hertz's derivation the electrons were assumed to make only elastic collisions with gas molecules and thus their velocities increase as they move into regions of more positive potential. There is thus a *thermal effusion* effect by which the electrons tend to move back against the field. The result is that the net drift is only 1/3 as great as if no increase of electron velocity occurred.

Assuming that the electrons start from the electrode (0) with a uniform velocity corresponding to V_0 volts, and that they suffer only elastic collisions with gas atoms, their velocity at any point is given by

$$(\tfrac{1}{2})mv^2 = (V + V_0)e \tag{2}$$

where V is the potential at the point relative to that of the emitting electrode.

Differentiating, we obtain

$$vdv = \frac{e}{m}\frac{dV}{dx}dx = \gamma dx$$

and the concentration gradient is thus

$$\frac{dn}{dx} = \frac{\gamma}{v}\frac{dn}{dv}. \tag{3}$$

Combining Eqs. (1) and (3), the drift velocity is

$$v_x = \frac{\gamma\lambda}{3}\left(\frac{1}{v} - \frac{1}{n}\frac{dn}{dv}\right) \tag{4}$$

It is not, in general, necessary that the maximum concentration gradient should lie in a direction coinciding with that of the maximum potential gradient. For the sake of simplicity, however, let us consider those cases in which at each point these two directions do coincide. The equipotential surfaces are then also surfaces of equal concentration n, and n is thus a single-valued function of V. We shall also restrict ourselves to cases in which the currents are so small that space charge effects are negligible, i.e., the potential distribution is given by integration of Laplace's equation.

Consider now a tube of force of small cross-section reaching from the emitting electrode (0) to a second electrode (1) which is at potential V_1. Let A be the cross-sectional area of the tube at any distance s measured along the tube and let L be the number of lines of force ($\int E_s dA$) contained in the tube.

Then

$$dV/ds = L/A. \tag{5}$$

The acceleration is then

$$\gamma = \frac{e}{m}\cdot\frac{L}{A}. \tag{6}$$

The drift current i_A along the tube of force is

$$i_A = Anev_s. \tag{7}$$

Therefore, combining Eqs. (6) and (7)

$$\frac{v_s}{\gamma} = \frac{i_A m}{ne^2 L}. \tag{8}$$

Substituting in Eq. (4) we obtain

$$\frac{3i_A m}{e^2 \lambda L} = \frac{n}{V} - \frac{dn}{dv}. \tag{9}$$

Assuming that the free path λ is the same throughout the length of the tube of force, then since i_A is also constant Eq. (9) may be integrated giving

$$n = \frac{3i_A mv}{e^2 \lambda L} \ln\left(\frac{c}{v}\right) \tag{10}$$

where c is a constant of integration.

To determine the integration constant we can insert the boundary condition that the concentration at the electrode 1 (anode) is zero.

Putting $n=0$ for $v=v_1$ we find $c=v_1$ and Eq. (10) becomes

$$n = \frac{3i_A mv}{e^2 L\lambda} \ln\left(\frac{v_1}{v}\right). \tag{11}$$

At any point in the gas the random current density[3] is

$$I_e = (\tfrac{1}{4})nev. \tag{12}$$

Inserting the value of n from Eq. (11) and expressing v in terms of V in accord with Eq. (2) we obtain

$$I_e = \frac{3}{4}\,\frac{i_A(V+V_0)}{L\lambda} \ln\left(\frac{V_1+V_0}{V+V_0}\right). \tag{13}$$

In Eq. (9), i_A and L are constant along the tube of force. We have, however, postulated that the equipotential surfaces lying between the two electrodes are identical with the surfaces of equal concentration and therefore n, v and dn/dv are constant over any equipotential surface. We see then by Eq. (9) that the ratio i_A/L, which is constant along any tube, must also have the

[3] See I. Langmuir and K. T. Compton, Rev. Mod. Phys. 3, 221 (1931).

same value for all tubes in the field and thus must be equal to i/L_t where i is the total current between the electrodes and L_t is the total number of lines of force passing between the electrodes.

If all the lines of force which emanate from one electrode pass to the other, i.e., if the algebraic sum of the charges of the two electrodes is zero, then

$$L_t = 4\pi V_1 C \tag{14}$$

where C is the electrostatic capacitance between the electrodes in cm.

Replacing i_A and L in Eq. (13) by i and L_t we thus obtain the result

$$I_e = \frac{3}{16\pi}\cdot\frac{i}{\lambda C}\cdot\left(\frac{V+V_0}{V_1}\right)\ln\left(\frac{V_1+V_0}{V+V_0}\right). \tag{15}$$

Let us denote by I_0 the random current density at the surface of the cathode as calculated from this equation, by placing $V=0$. In order that the presence of the electrode shall be compatible with the conditions that we have assumed in the neighboring gas it is clearly necessary that the electrode should emit electrons (of uniform velocity corresponding to V_0 volts) with a *uniform current density* I_0 which thus corresponds to the saturation current density. The electrons must also be emitted in random directions, i.e., according to Lambert's cosine law.

If we have an emitting electrode which fulfils these conditions, we may thus calculate the current i that passes to the anode:

$$i = \frac{16\pi}{3} I_0 \lambda C \phi \tag{16}$$

where the function ϕ is defined by

$$\phi = \frac{V_1/V_0}{\ln\left(\dfrac{V_0+V_1}{V_0}\right)} \tag{17}$$

Values of ϕ for various values of V_1/V_0 are given in Table I.

TABLE I. *Currents produced by electrons emitted with uniform velocity. ϕ is defined by Eqs. (16) and (17).*

V_1/V_0	ϕ	V_1/V_0	ϕ	V_1/V_0	ϕ
−1.0	0	0.1	1.049	3	2.165
−0.99	0.206	0.2	1.097	4	2.480
−0.9	0.390	0.3	1.140	5	2.79
−0.8	0.496	0.4	1.189	6	3.08
−0.6	0.655	0.6	1.276	8	3.64
−0.4	0.784	0.8	1.360	10	4.16
−0.2	0.895	1.0	1.445	15	5.42
−0.1	0.949	1.5	1.637	20	6.58
0	1.000	2.0	1.820	30	8.75

As the anode voltage is raised the current increases in proportion to ϕ. Since the electrons are emitted with velocities corresponding to V_0 volts, the

anode current falls to zero only when a *retarding* voltage of V_0 volts is applied. With accelerating voltages the current increases slowly but continuously.

If both electrodes emit electrons with velocity V_0 and if the potential of one with respect to the other lies between $-V_0$ and $+V_0$, the current must flow both ways so that the net current is to be obtained by applying Eq. (16) for each electrode in turn and taking the difference of these two currents (or algebraic sum). When the voltage lies outside of the range $-V_0$ to $+V_0$, one or the other of the currents becomes zero so that a single application of Eq. (16) suffices.

It should be kept in mind that Eq. (16) is strictly applicable only at such high pressures that the electron free path is small compared to the distance between the electrodes. Otherwise the boundary conditions which we have used, such as $n=0$ at the anode, are not valid.

We have seen that it was necessary for us to assume that I_0 is uniform over the cathode surface. If this condition is not fulfilled the surfaces of equal concentration no longer coincide with the equipotential surfaces and the problem of the current flow is then far more complicated than for the case we have treated.

It is also clear for the same reason that the foregoing method is not appliable when there are *two anodes* at different potentials. This difficulty is apparent when we consider that according to our procedure n must be placed equal to zero at each of these surfaces, although they are at different potentials. This violates our postulate that n is a single valued function of V. Two anodes at the same potential may, of course, be regarded as a single anode and Eqs. (16) and (17) are then applicable.

Practical applications of Eq. (16) will usually be made with electrodes of simple shapes. Substituting the well-known expressions for the capacitance[4] in Eq. (16) we obtain:

For *parallel planes*, the net current per unit area flowing between the electrodes is

$$I_x = (4/3)I_0\phi\lambda/a. \tag{18}$$

The current that flows is thus inversely proportional to the pressure and at high pressures may be very small compared to the saturation electron emission I_0.

For *coaxial cylinders* the net current per unit length is

$$i_L = (8\pi/3)I_0\phi\lambda/\ln(r_1/r_0). \tag{19}$$

Here I_0 is the current density of the electron emission corresponding to saturation from the *emitting electrode* regardless of whether this is the outer or the inner cylinder. The radii of the cylinders are r_1 and r_0.

For *concentric spheres* the total current is

$$i = (16\pi/3)I_0\phi\lambda r_0 r_1/(r_1 - r_0). \tag{20}$$

[4] See p. 198 of reference 3.

It should be noted that if the *saturation current density* I_0 from the inner and the outer cylindrical (or spherical) electrodes are equal, the actual currents remain unchanged if the relative polarity of the electrodes is reversed, although the total saturation currents, if they could be obtained, would be proportional to the areas of the emitting electrodes. This conclusion can readily be tested by experiment.

The source of the electrons from the emitting electrode may be one of many kinds, for example, photoelectric or thermionic. A case of particular interest in connection with a study of the un-ionized (or weakly ionized) regions beyond the end of a neon arc[1] is the liberation of high velocity electrons (*ca.* 10 volts) from the surfaces of electrodes by the action of metastable atoms which diffuse to these electrodes. The metastable atoms are generated throughout the gas by the action of ultraviolet light (broadened resonance lines) from the arc, at a rate proportional to the inverse cube of the distance from the end of the arc. Let us calculate the relative current densities I_0 of emitted electrons from the inner and outer cylinders under these conditions.

If the electrodes are at a considerable distance from the end of the arc and the radiation passes parallel to the axis, then within the space between two cylindrical electrodes of short lengths we may assume a uniform rate of production of metastable atoms. The diffusion of these to the two electrodes is a problem essentially similar to that[5] of the potential distribution between cylinders if the space contains a uniform space charge ρ.

Imposing the boundary conditions $V=0$ at the surface of both cylinders, we find that the potential gradient at any point of radius r is

$$\frac{dV}{dr} = \pi\rho\left[\frac{(r_2^2 - r_1^2)}{r \ln (r_2/r_1)} - 2r\right] \tag{21}$$

where r_2 and r_1 are the radii of the outer and inner cylinders respectively. By substituting first $r=r_1$ and then $r=r_2$ we find the potential gradients at the surfaces of the two electrodes. The ratio of these two gradients is equal to the ratio of the corresponding rates of arrival of metastable atoms *per unit area* and therefore should be proportional to the ratio I_1/I_2 of the saturation current densities (I_0) of the emitted electrons from the two electrodes. In this way we find

$$\frac{I_1}{I_2} = \frac{r_2[r_2^2 - r_1^2 - 2r_1^2 \ln (r_2/r_1)]}{r_1[r_2^2 - r_1^2 - 2r_2^2 \ln (r_2/r_1)]}. \tag{22}$$

For example, if $r_2/r_1=10$ this gives $I_1/I_2=-2.62$ (the negative sign merely indicates that the currents flow in opposite directions).

The corresponding equation for concentric spheres is

$$\frac{I_1}{I_2} = -\frac{r_2(r_2 + 2r_1)}{r_1(r_1 + 2r_2)} \tag{23}$$

which gives $I_1/I_2=-5.72$ when $r_2/r_1=10$.

[5] See p. 213 of reference 3.

Thus we see that the current density I_0 at the inner electrode is greater than at the outer electrode if the electrons owe their origin to metastable atoms produced uniformly throughout the gas. It therefore follows from Eq. (19) that the net current will be greater (2.62 fold for $r_2/r_1=10$) when the small inner cylindrical electrode is cathode than when the larger electrode is cathode, although if the currents were saturated the current in the former case would be smaller instead of larger (0.26 instead of 2.6 fold).

We have thus far assumed that all the electrons are emitted with the same velocity V_0 volts. Although this may be roughly true for electrons emitted under the influence of metastable atoms, it will certainly not be a satisfactory approximation for thermal emission of electrons. By summation of the currents from each velocity group, we may calculate the net current produced by a Maxwellian velocity distribution.

The total number of electrons per unit volume which have speeds (irrespective of direction) lying between c and $c+dc$ is given by[6]

$$4\pi n(m/2\pi kT)^{3/2} \exp(-mc^2/2kT)c^2dc.$$

Because of the relation expressed by Eq. (12) it follows that the contribution of these electrons to the random current density crossing any given plane is

$$dI = \pi en(m/2\pi kT)^{3/2} \exp(-mc^2/2kT)c^3dc. \tag{24}$$

Applying this to the surface of an electrode which emits electrons with a Maxwellian velocity ditribution corresponding to temperature T and current density I_0, and integrating from $c=0$ to $c=\infty$ we find

$$I_0 = ne(kT/2\pi m)^{1/2} \tag{25}$$

Eliminating n between Eqs. (24) and (25) we obtain

$$dI = I_0\epsilon^{-\eta_0}\eta_0 d\eta_0 \tag{26}$$

where

$$\eta_0 = mc^2/2kT = V_0e/kT = 11600V_0/T \tag{27}$$

if V_0 is the emission velocity in volts.

To calculate the net current between the two electrodes, we may insert the value of dI in place of I_0 in Eq. (16) and integrate from $\eta_0=0$ to $\eta_0=\infty$.

In this integration the value of ϕ is obtained from Eq. (17) by placing

$$V_1/V_0 = \eta/\eta_0$$

which by Eq. (27) is equivalent to

$$\eta = V_1e/kT = 11600V_1/T \tag{28}$$

if V_1 is in volts.

[6] This is obtained from Eq. (71) of Compton and Langmuir's article, Rev. Mod. Phys. **2**, 205 (1930), by replacing h by $1/2kT$.

In this way we find

$$i = (16\pi/3) I_0 \lambda c \phi_T \tag{29}$$

where

$$\left.\begin{aligned} \phi_T &= \eta \int_0^\infty \frac{\epsilon^{-x} dx}{\ln (1 + \eta/x)} \quad \text{if } \eta > 0 \\ \text{or} \qquad \phi_T &= \eta \int_{-\eta}^\infty \frac{\epsilon^{-x} dx}{\ln (1 + \eta/x)} \quad \text{if } \eta < 0 \end{aligned}\right\} \tag{30}$$

The reason that the lower limit of integration must be changed when η is negative is that electrons whose initial velocities give $\eta_0 < -\eta$ cannot reach the collector.

TABLE II. *Currents produced by electrons emitted with Maxwellian velocities at temperature T; ϕ_T is defined by Eqs. (29) and (30); η is given by Eq. (28).*

η	ϕ_T	η	ϕ_T	η	ϕ_T
−4	0.042	−0.2	0.892	4	2.358
−3	0.100	0	1.000	6	2.908
−2	0.236	+0.1	1.034	8	3.421
−1	0.516	0.5	1.217	10	3.913
−0.8	0.600	1	1.408	20	5.895
−0.6	0.688	2	1.748	30	8.170
−0.4	0.787	3	2.051	50	11.892

The values of η given in Table II have been calculated from Eqs. (30) by Simpson's rule or by series expansion. They are believed to be accurate within one or two units in the last figure. Comparison with Table I shows that for values of η and V_1/V_0 which are equal, the values of ϕ_T and ϕ are very nearly equal when η is greater than about -0.6. By Eq. (28) we see that this means that, except for large negative voltages, no great error is made if the thermally emitted electrons are considered to have a uniform energy corresponding to $T/11600$ volts.

Experiments which will probably be described in a paper by C. G. Found and the writer have given results which are explicable in terms of the theories here presented. The writer is much indebted to Mr. Found for assistance in the preparation of this paper.

THE AVERAGE LIFE OF THE IONIZED HELIUM ATOM

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Abstract

Review of the theory in relationship to ionized helium:—From the results of previous workers it is shown that the theoretical values for the average life of energy levels of ionized helium are 1/16th as long as the life-time of the same levels of hydrogen. A table of average lives for ionized helium is given which shows that the average life becomes progressively greater for higher quantum states.

Experimental method for measuring the average life:—Electrons in helium at low pressure were confined into a narrow beam by a longitudinal magnetic field. A transverse electric field drew out the ions formed in the beam. The light was projected on the slit of a spectrograph with the direction of motion of the ions parallel to the slit. Formulas giving the intensity of the displaced spark line as a function of its distance from the center of the electron beam have been derived previously. The average life can be obtained from the measurements of the amount of the displacements of the region of maximum intensity of the spark line from the center of the beam.

Experimental results and comparison with the theory:—(1) A comparison of displacements for the first four lines of the "4686" series of He^+ show that the average life becomes progressively greater for the higher quantum states in agreement with the theory. (2) Results obtained for the line 2733A 6→3 give an average life of $1.1 \pm 0.2 \times 10^{-8}$ sec. for the sixth quantum state in good agreement with 1.17×10^{-8} sec. the theoretical value for the mean average life of this level. (3) As the voltage of the electrons in the beam was increased the measured average life became greater which showed the presence of transitions into the sixth state from the higher quantum levels. (4) An alternative method for interpretating the experimental results is given which does not assume a free interchange among the sublevels. The theoretical intensity distribution of each of the five fine structure lines which make up the unresolved line 2733A is calculated. It is found that the resultant intensity distribution is almost exactly the same as the intensity distribution calculated for the case of free interchange or in other words for the case of a single exponential decay law. The experimental intensity curve agrees with the theoretical curve.

Discrepancies existing among authors for values of the matrix amplitude squared for hydrogen:—On comparing the values for the matrix amplitudes squared for hydrogen obtained by different authors, it is found that the values obtained by Slack and Kupper are in disagreement for the following transitions: $5_1 \rightarrow 4_2$, $6_1 \rightarrow 4_2$, $5_0 \rightarrow 4_1$, $6_0 \rightarrow 4_1$, $6_3 \rightarrow 5_4$, $6_0 \rightarrow 5_1$, $6_3 \rightarrow 5_4$, $6_2 \rightarrow 4_3$. These discrepancies do not greatly affect the theoretical value for the mean average life of the sixth quantum state, or the alternative method for interpretating the experimental results.

Effect of electron spin:—It is proved that the electron spin corrections do not alter the theoretical interpretation of the experimental results, because it is shown that the average life of the n, l, j, m state is independent of j, and m, and equal to the average life in the nonspin theory of the n, l, m state, independent of m, and also that the mean average life is independent of spin.

ONE of the important quantities which can be calculated from the quantum theory is the average rate of radiation of energy produced by transitions occurring in atoms. Theoretical considerations give directly the prob-

ability of transition and consequently the average lifetime in the initial states. It becomes possible, therefore, to test the theory by comparison with experiments which give numerical results for the average lives of excited states. The present work deals with the measurement of the average life for ionized helium. It is possible to obtain a direct comparison between the absolute values of the average life as obtained from the experiment and from the theory.

PART I. THE THEORY

Since the experimental method used for determining the average life is limited to those emitters which are ions, it is advisable to deal with ionized helium which is the simplest type of ion and one which can be treated theoretically in the same manner as hydrogen.

The average life of an excited state is equal numerically to the reciprocal of the sum of the transition probabilities corresponding to all of the possible transitions which can take place from the level concerned. Expressed analytically, the average life $T(n, l, m)$ of the state n, l, m is given by

$$T(n, l, m) = \frac{1}{\sum_{n', l', m'} A_{n,l,m}^{n',l',m'}}$$

where $A_{n,l,m}^{n',l',m'}$ is the probability of a transition from state n, l, m to state n', l', m'. This summation is extended over all of the lower states. We see from this equation that in order to obtain a numerical value for the average life a knowledge of the numerical values of all the transition probabilities is essential. Schrödinger[1] quotes a formula for the total intensities of the lines in the Lyman and Balmer series given to him by Pauli, and capable of giving the transition probabilities. Sugiura[2] has calculated the transition probabilities for a number of the lines of the Paschen, Balmer and Lyman series lines of hydrogen. In a later paper[3] he also considered the more general case of the transition probability between two states in a field with a central charge Ze. Slack,[4] using a formula obtained by Sommerfeld and Unsöld, has prepared a table of transition probabilities for a large number of transitions for hydrogen. Kupper,[5] also, has calculated the values for the matrix amplitudes squared for many transitions in hydrogen.

It is well known that from the classical theory the average energy radiated per unit time is given by

$$-\frac{\overline{dE}}{dt} = \frac{64\pi^4\nu^4}{3c^3}\left| P_1 \right|^2$$

[1] Schrödinger, Ann. d. Physik **80,** 437 (1926) for the formula of W. Pauli.

[2] Sugiura, Jour. d. Physique **8,** 113 (1927).

[3] Sugiura, Scientific Papers of the Institute of Physical and Chemical Research (Tokyo) No. 193, June 25, 1929.

[4] Slack, Phys. Rev. **31,** 527 (1928).

[5] Kupper, Ann. d. Physik **86,** 511 (1928).

where the electrical moment P of the classical vibration is written in the exponential form $P=P_1e^{2\pi i\nu t}+P_{-1}e^{-2\pi i\nu t}$. Utilizing this expression directly in the quantum theory, we have the following for the value of the transition probability,[6]

$$A^{n',l',m'}_{n,l,m}=\frac{64\pi^4e^2\nu^3{}^{n',l',m'}_{n,l,m}\left|J^{n',l',m'}_{n,l,m}\right|^2}{3c^3h} \tag{1}$$

where $J^{n',l',m'}_{n,l,m}$ is the vector matrix amplitude given by

$$\left|J^{n',l',m'}_{n,l,m}\right|^2=\left|x^{n',l',m'}_{n,l,m}\right|^2+\left|y^{n',l',m'}_{n,l,m}\right|^2+\left|z^{n',l',m'}_{n,l,m}\right|^2$$

with the matrix elements $(x, y, z)^{n',l',m'}_{n,l,m}$ expressed in terms of the normalized wave functions $\psi_{n,l,m}\psi_{n',l',m'}$ in the following form:

$$\left.\begin{matrix}x\\y\\z\end{matrix}\right\}^{n',l',m'}_{n,l,m}=\int\begin{matrix}x\\y\\z\end{matrix}\psi_{n,l,m}\,\psi^*_{n',l',m'}d\tau.$$

Since we are not interested in each matrix element component for different magnetic quantum numbers m the expression $\sum^m\sum_{m'}\left|J^{n',l',m'}_{n,l,m}\right|^2$ is evaluated. From (1) we obtain

$$\sum_m\sum_{m'}A^{n',l',m'}_{n,l,m}=\frac{64\pi^4\nu^3{}^{n',l'}_{n,l}\,e^2\sum_m\sum_{m'}\left|J^{n',l',m'}_{n,l,m}\right|^2}{3c^3h}.$$

Sugiura defines the quantity $A^{n',l'}_{n,l}$, as the mean probability of a transition by the following formula;

$$A^{n',l'}_{n,l}=\frac{\sum_m\sum_{m'}A^{n',l',m'}_{n,l,m}}{g_l} \tag{2}$$

where $g_l=2l+1$ is the number of magnetic levels or the statistical weight of the lth level. This equation can be thought of as defining the transition probability which determines the rate at which energy is radiated from the magnetic levels of the initial states. It is the reciprocal of this expression which gives the average life, and also the quantity which when multiplied by g_l will give the total rate at which energy is radiated from all the magnetic levels and consequently give the intensity of the spectrum line. From the summation-rule for the Zeeman components we see that $A^{n',l'}_{n,l}$ is also equal to $\sum^{m'}A^{n',l',m'}_{n,l,m}$ independent of m.

From Eqs. (1) and (2) we have the final expression for the transition probability $A^{n',l'}_{n,l}$ as defined above,

$$A^{n',l'}_{n,l}=\frac{64\pi^4\nu^3{}^{n',l'}_{n,l}e^2\sum_m\sum_{m'}\left|J^{n',l',m'}_{n,l,m}\right|^2}{3c^3hg_l}. \tag{3}$$

[6] See for instance, Sugiura, reference 2.

Sugiura has evaluated this quantity by obtaining the following expression for the matrix amplitude squared for the case of a central charge Ze and for a transition from state n, l to n', l'

$$\sum_{m}\sum_{m'}|J_{n,l,m}^{n',l',m'}|^2 = \left(\frac{a_0}{4Z}\right)^2 l''\frac{(n-l-1)!(n'-l'-1)![(l+l'+3)!]^2}{(n+l)!(n'+l')!} \left(\frac{2n}{n+n'}\right)^{2(l'+2)}\left(\frac{2n'}{n+n'}\right)^{2(l+2)}(C_{n,l}^{n',l'})^2 \tag{4}$$

where $C_{n,l}^{n',l'}$ is the coefficient of $y_1^{n-l-1}y_2^{n'-l'-1}$ in the expansion of

$$\frac{(1-y_1)^{l'-l+2}(1-y_2)^{l-l'+2}}{\left(1-y_1y_2-\frac{n-n'}{n+n'}y_1+\frac{n-n'}{n+n'}y_2\right)^{l+l'+4}}$$

and l'' is the greater value of l and l', $a_0 = h^2/4\pi^2me^2$. Therefore we see from this equation that the matrix amplitude squared is inversely proportional to Z^2 for any given transition. Taking into account that ν^3 is directly proportional to Z^6 we see from Eq. (3) that $A_{n,l}^{n',l'}$ is directly proportional to Z^4.[7] Thus, in the case of ionized helium the values of the transition probabilities are 16 times greater than the values for the same transitions in hydrogen. This means that the average life of the levels in ionized helium will be 1/16th as long as the average life-time of the same levels in hydrogen. Consequently, for the purpose of calculating the average life for ionized helium we can use directly numerical values for the transition probabilities for hydrogen.

The mean average life.

The substates corresponding to different l values for a given value of n have for the relativistic case, energies which differ from each other only by a very small amount, so that it is impractical to separate the different fine structure lines in the measurements of the average life.

Sugiura has calculated a mean average life $T(n) = 1/\sum_{n'} A_n^{n'}$ which can be used for comparison with experiments provided that there exists free interchange or statistical equilibrium among the various sublevels of the nth state. $A_n^{n'}$ is the average rate of transition from the state n to n' and is given by

$$A_n^{n'} = \frac{\sum_{l,l'} g_l A_{n,l}^{n',l'}}{\sum_l g_l}$$

[7] See also Sommerfeld, Atombau and Spektrallinen (Wellenmechanischer Ergänzungsfand) p. 96.

and is called by Slack the total probability of line emission from n to n'. The intensity of the unresolved line will diminish *exponentially** with the time, and the decay time $T(n)$ will be given by

$$T(n) = \frac{\sum_l g_l}{\sum_l \sum_{n',l'} g_l A_{n,l}^{n',l'}} . \tag{5}$$

* Although it is perhaps obvious that the unresolved line will diminish exponentially with the time on account of averaging the rates of transitions, however it can be shown analytically to be true in the following manner:

Let $n_{n,l}(t)$ be the number of electrons in the n, l, state. We shall assume that

$$n_{n,l}(t) = f_n(t) g_l \tag{A}$$

where as before $g_l = 2l+1$ (the number of magnetic levels) and $f_n(t)$ a factor of proportionality which is independent of l. Therefore, $N_n(t)$ the total number of electrons in the nth state is given by

$$N_n(t) = \sum_l n_{n,l}(t) = f_n(t) \sum_l g_l . \tag{B}$$

The rate at which electrons leave the n, lth state to go to lower states n', l' is given by

$$\frac{dn_{n,l}(t)}{dt} = - \sum_{n',l'} A_{n,l}^{n',l'} \, n_{n,l}(t) .$$

$$\therefore \frac{dN_n(t)}{dt} = \sum_l \frac{dn_{n,l}(t)}{dt} = - \sum_l \sum_{n',l'} A_{n,l}^{n',l'} \, n_{n,l}(t)$$

By virtue of (A) we see that

$$\frac{dN_n(t)}{dt} = - \frac{\left(f_n(t) \sum_l g_l \right) \sum_l \sum_{n',l'} A_{n,l}^{n',l'} g_l}{\sum_l g_l} .$$

Utilizing Eq. (B), leaves

$$\frac{dN_n(t)}{dt} = - \frac{N_n(t) \sum_l \sum_{n',l'} A_{n,l}^{n',l'} g_l}{\sum_l g_l} .$$

Therefore, we have on integrating, the following

$$N_n(t) = N_n(0) e \exp - \left(\frac{\sum_l \sum_{n',l'} A_{n,l}^{n',l'} g_l}{\sum_l g_l} \right) t .$$

From Eqs. (A), (B), and (C) we find that

$$n_{nl}(t) = \frac{N_n(0) g_l}{\sum_l g_l} e \exp - \left(\frac{\sum_l \sum_{n',l'} A_{n,l}^{n,'l'} g_l}{\sum_l g_l} \right) t .$$

Therefore, the intensity of the spectrum line corresponding to a transition from state n to n' is given by

$$I_n^n(t) = \sum_l \sum_{l'} I_{n,l}^{n',l'}(t) = \left[\sum_l \sum_{l'} \frac{g_l A_{n,l}^{n',l} h\nu_{n,l}^{n',l'} N_n(0)}{\sum g_l} \right] e \exp - \left[\frac{\sum_l \sum_{n',l'} A_{n,l}^{n',l'} g_l}{\sum_l g_l} \right] t$$

We see, from this equation, that the intensity of the unresolved line willl diminish exponentially with the time, having a decay time the same as that given above for $T(n)$.

Effect of electron spin.

A similar expression for the mean average life $T'(n)$ can be written at once taking into account electron spin.

$$T'(n) = \frac{\sum_{l,j} g_{l,j}}{\sum_{l,j} \sum_{n',l',j'} g_{l,j} A^{n',l',j'}_{n,l,j}} . \tag{6}$$

To determine the effect of electron spin on the values of the average lives, let us consider the general proof that the spin corrections will not effect the intensity.[8] From the general theorem of spectroscopic stability[9]

$$\sum_{j,m,j'm'} | J^{n',l',j'm'}_{n,l,j,m} |^2 = \sum_{m_s,m_l,m_s',m_l'} | J^{n',l',m_s',m_l'}_{n,l,m_s,m_l} |^2 .$$

The left hand side has the usual spin coupling while the amplitudes on the right hand side result when the spin is completely decoupled and has separate spacial quantization. The matrix elements on the right side are completely independent of m_s i.e.

$$X^{n',l',m_s'm_l'}_{n,l,m_s,m_l} = \delta^{m_s'}_{m_s} X^{n',l',m_l'}_{n,l,m_l} ,$$

similarly for the y and z components, where

$$| X^{n'l'j'm'}_{n,l,j,m} |^2 + | Y^{n',l',j'm'}_{n,l,j,m} |^2 + | Z^{n'l'j'm'}_{n,l,j,m} |^2 = | J^{n',l',j'm'}_{n,l,j,m} |^2$$

The sum-rule assures that $\sum_{j'm'} |J^{n',l',j',m'}_{n,l,j,m}|^2$ is independent of j, m, and $\sum_{m'l} J^{n',l',m'l}_{n,l,m_l}$ of m_l. Since there are $(2L+1)$ $(2S+1)$ values of j, m, or m_l, m_s we have

$$(2S+1)(2L+1) \sum_{j'm'} | J^{n',l',j',m'}_{n,l,j,m} |^2 = (2S+1)(2L+1) \sum_{m_l'} | J^{n',l',m_l'}_{n,l,m_l} |^2 .$$

On cancelling out the factor $(2L+1)$ $(2S+1)$ we have the desired result. In addition, if we sum over n' and l' then it is proved at once that the *average life of the n, l, j, m state is independent of j, and m, and equal to the average life in the nonspin theory of the n, l, m state independent of m.***

By virtue of the above theorem we can write at once that

$$A^{n',l'}_{n,l} = \frac{\sum_{j,j'} g_{l,j} A^{n',l',j'}_{n,l,j}}{\sum_{j} g_{l,j}}$$

also

$$g_l = \tfrac{1}{2} \sum_j g_{l,j} .$$

[8] The writer is indebted to Professor J. H. Van Vleck for this proof.

[9] Cf. for instance Van Vleck, Phys. Rev. **29**, 740 (1927).

** In this connection Sugiura has previously mentioned that the decay constants or average lives for the n, l terms are necessarily independent of j as long as the sum-rule holds.

By use of these equations it is seen at once from (5) and (6) that $T(n) = T'(n)$. Therefore, *the mean average life is independent of the spin corrections.*

In Table I are given theoretical values for the average lives and the mean average lives for levels up to and including the seventh state of ionized

TABLE I. *Theoretical values of the average life of ionized helium.*

Level	Average life	Mean average life
n_l	$T(n, l)$, (sec.)	$T(n)$, (sec.)
1_0		
2_0		
2_1	1.02×10^{-10}	1.36×10^{-10}
3_0	1.01×10^{-8}	
3_1	3.38×10^{-10}	6.4×10^{-10}
3_2	9.93×10^{-10}	
4_0	1.456×10^{-8}	
4_1	7.89×10^{-10}	2.127×10^{-9}
4_2	2.320×10^{-9}	
4_3	4.66×10^{-9}	
5_0	1.82×10^{-8}	
5_1	1.49×10^{-9}	
5_2	4.33×10^{-9}	5.38×10^{-9}
5_3	8.73×10^{-9}	
5_4	1.45×10^{-8}	
6_0	2.576×10^{-8}	
6_1	2.443×10^{-9}	
6_2	7.196×10^{-9}	1.178×10^{-8}
6_3	1.471×10^{-8}	
6_4	2.682×10^{-8}	
6_5	3.906×10^{-8}	
7_0	3.286×10^{-8}	
7_1	3.647×10^{-9}	
7_2	1.175×10^{-8}	
7_3	2.141×10^{-8}	2.237×10^{-8}
7_4	3.373×10^{-8}	
7_5	6.449×10^{-8}	
7_6	8.802×10^{-8}	

helium. These values for levels up to and including the fourth state were taken from a similar table prepared by Sugiura for hydrogen. The present values for ionized helium differ by a factor of 16 from those for hydrogen for the reason given above. Since Sugiura's table does not include levels higher than the fourth, the values of the average lives for the fifth, sixth and seventh states were obtained from Slack's table of transition probabilities for hydrogen. These transition probabilities as obtained by Slack were multiplied by 16 to give the average life for ionized helium as listed in the table.

Discrepancies existing among the values of the matrix amplitude squared for hydrogen obtained by different authors.

A comparison has been made between the values of the matrix amplitude squared as obtained by Sugiura,[2] Slack[4] and Kupper.[5] For all the transitions

from the second, third and fourth quantum states, the values obtained by the different authors are in good agreement.

For the case of the transitions from the fifth state, Slack's and Kupper's values are in agreement with the exception of the transitions $5_1 \rightarrow 4_2$ and $5_0 \rightarrow 4_1$. For the transitions from the sixth quantum state, Slack's and Kupper's results disagree for the following transitions: $6_1 \rightarrow 4_2$, $6_0 \rightarrow 4_1$, $6_5 \rightarrow 5_4$, $6_0 \rightarrow 5_1$, $6_3 \rightarrow 5_4$, and $6_2 \rightarrow 4_3$. Table II has been prepared showing the values of the matrix amplitudes squared for the above transitions.

In the third column are given values calculated from Kupper's "Spezielle Serien" formulae. For example, Kupper gives for the $n_0 \rightarrow 4_1$. $(4P-nS)$ transition the following formula:

$$\frac{2^{21}n^9(n-4)^{2n-10}(57n^4-38n^2+80)^2}{3(n+4)^{2n+10}}.$$

If we use the more general formula given by Kupper, called the "Allgemeine Formeln der Seriengruppen $n-l-1=D'$ $(n'>n)$" we obtain for the $n_0 \rightarrow 4_1$ transition a different quantity:

$$\frac{2^{21}n^9(n-4)^{2n-10}(57n^4-608n^2+1280)^2}{5\times 3(n+4)^{2n+10}}$$

which is evaluated numerically in the fourth column in Table II. For the $6_0 \rightarrow 4_1$ transition this formula gives 1.59 which is the same value that is obtained from Sugiura's formula. Also it agrees well with Slack's values of 1.88 but is in disagreement with 14.8 the value obtained by Kupper's special series formula. For the $5_0 \rightarrow 4_1$ transition the agreement is not as good, as illustrated in Table II.

TABLE II. *Comparison of values for the matrix amplitude squared for hydrogen.*[10]

Transition	Kupper's table	Calculated from Kupper's special series formula	Calculated from Kupper's general formula	Calculated from Sugiura's formula	Calculated from Slack's table
$5_1 \rightarrow 4_2$	9.1				0.094
$6_1 \rightarrow 4_2$	1.21	1.26			0.013
$5_0 \rightarrow 4_1$	105.	135.	10.58		21.0
$6_0 \rightarrow 4_1$	14.8	14.8	1.59	1.59	1.88
$6_5 \rightarrow 5_4$	201.	1851.		1851.	1822.
$6_0 \rightarrow 5_1$	247.				77.60
$6_3 \rightarrow 5_4$	8.2				12.3
$6_2 \rightarrow 4_3$	0.48				0.284

These discrepancies do not appreciably effect the theoretical value for the mean average life of the sixth quantum state.

PART II. THE EXPERIMENT

The experimental method used in the present work for measuring the average life is similar to that previously described by the writer[11] for the case

[10] The values here are $\frac{1}{2}$ the values given by Sugiura's formula of Eq. (4).

[11] Maxwell, Phys. Rev. **32**, 721 (1928).

of an election beam of nonuniform current density. It is necessary to modify slightly the derivation used previously by taking into account the more general case where there are a large number of levels involved instead of the simple case of two levels as treated before.

On referring to the previous work we see that if δn is the number of excited ions per second leaving the volume element dv lying between ξ and $\xi+d\xi$ then $\delta n e^{-\beta t(x,\xi)}$ is the number of these which will arrive at a distance x from the lower edge of the beam without becoming deexcited, where $t(x, \xi) = [2m(x-\xi)/Xe]^{1/2}$ is the time required for the ion to go from ξ to x. β is the reciprocal of the average life of the level n_l given by

$$1/\beta = T(n, l) = 1/\sum_{n',l'} A_{n,l}^{n'l'}.$$

Now the number of transitions which take place from state n, l to n', l' in volume element dA lying between x and $x+dx$ in time dt while the ions move the distance dx is

$$-d_{n,l}^{n',l'}(\delta n e^{-\beta(n,l)t(x,\xi)}) = A_{n,l}^{n',l'}\delta n e^{-\beta(n,l)t(x,\xi)}\frac{\partial t}{\partial x}dx.$$

This corresponds to a similar expression for the number of transitions occurring per second in dA obtained previously in which β has now been replaced by $A_{n,l}^{n',l'}$. The subsequent integration is unchanged so that the intensity formulas remain the same, except that they must now be multiplied by $g_l A_{n,l}^{n',l'}/\beta(n, l)$. For the previous case, this factor was obviously equal to unity. The introduction of the statistical weight g_l takes into account the case in which all the magnetic levels for a given n term have the same probability of excitation. The equation locating the maximum of the intensity curve is given by

$$2e^{-[(1/T(n,l))][2mx'/Xe]^{1/2}} - e^{-[1/T(n,l)][2m(a+x')/Xe]^{1/2}} - 1 = 0 \qquad (7)$$

This is the equation from which it is possible to determine the average life $T(n, l)$ after measuring experimentally the displacement x' of the maximum of the intensity curve.

Experimental arrangement.

The experimental arrangement used, showing the electrodes, and the electrical diagram are given in Fig. 1. The electrodes were mounted in a tube through which helium was circulated at a low pressure. The parts were made of molybdenum because it has nonmagnetic properties and because it does not give out occluded gases. The source of electrons was a 7 mil diameter tungsten filament whose cross section is indicated at F in the figure. Placed directly in front of the filament was the circular electrode 1 with a rectangular opening at its center of dimensions 0.6 mm by 4 mm. The filament 18 mm long, was in alignment with this opening, so that only electrons produced over 4 mm of its central portion were capable of being accelerated through the electrode 2 by potential V_1. The opening in electrode 2 was 2.75 mm by

6.0 mm. The electrons did not touch the edges of this opening because they were collimated into a narrow beam by an external magnetic field H of 2520 gauss applied in the direction of the accelerating electric field. The electrons passed between the electrodes 3 and 4 between which was applied an electric field which served to draw the ions out of the beam. The ions moved in a direction perpendicular to the direction of the electron beam. The magnetic field maintained the electron beam in spite of the cross electric field. The electrons then passed through electrodes 5 and were finally collected by 6 after receiving an additional amount of energy from the battery D. This procedure prevented secondary electrons from returning into the region between 3 and 4.

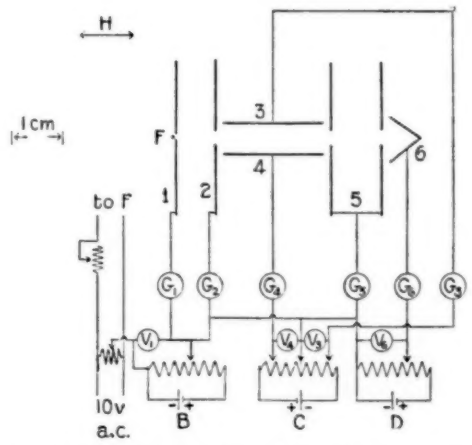

Fig. 1. Arrangement of electrodes and electric circuit.

The electrical circuit shows how the various potentials were applied. Battery B with its resistances produced the accelerating potentials while C served to maintain the transverse electric field. The potentials V_3 and V_4 could be arranged so that the space between 3 and 4 occupied by the electron beam was kept at any potential desired relative to the potential of 2. The filament was heated by a 60 cycle alternating current, so that it was not distorted by the force exerted on it by the magnetic field.

The light emitted from the region between 3 and 4 was projected on to the slit of the spectrograph with the image of the beam perpendicular to the slit. The direction of motion of the ions was then parallel to the slit. The distribution of density of the lines of ionized helium would be displaced in the direction of the motion of the emitters. The arc lines on the other hand would be undisplaced and furnished a reference point locating the center of the beam.

Fig. 2 shows the arrangement of the parts in the tube relative to the position of the spectrograph. The filament F was held firmly in position by large clamps made of tantalum. This prevented any large vibrations of the filament due to interaction of the alternating heating current and the external magnetic field. The shape of the electron beam is determined largely

by the size of the filament. The actual beam was 4 mm deep and approximately 0.4 mm wide. The light emitted from the region between 3 and 4 passed through the quartz window Q and was projected by the quartz lens L on to the slit S of the Hilger E_4 quartz spectrograph, in the manner described above. The lens was focused with respect to the center of the electron beam. This produced, with a magnification of 1.26 times, an image of depth 6.32 mm whose center lay in the plane of S. The spectrograph used was capable of bringing to focus the parts of the image of the beam outside of this plane. The magnification of the spectrograph for the wave-length 2733A for example, was practically unity, so that the total magnification in this case was 1.26 times.

The helium was purified by a glow discharge between iron and misch metal electrodes. It was then drawn through an adjustable leak and a liquid

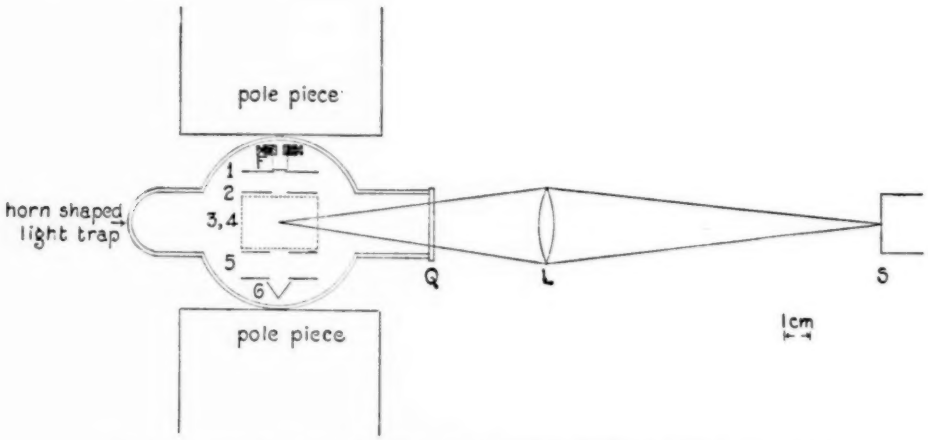

Fig. 2. A cross section showing arrangement of electrodes with respect to the position of the spectrograph.

air trap into the experimental tube and pumped finally back again into the purifier. The pressure in the experimental tube was generally maintained at 0.01 mm of Hg which means that the mean free path at this pressure was 2 cm for the atoms and about 10 cm for the electrons. This pressure was sufficient to produce enough excitation for simultaneous ionization and excitation. The mean free path of the helium ions was great enough so that they suffered practically no collisions before radiating. Thus de-excitation by collisions was prevented.

Results and Discussion

The dependence of the average life upon the state of excitation.

Fig. 3 shows results for the first four lines of the "4686" series of ionized helium obtained in some preliminary experiments in which a different type of filament and slit system were used than were illustrated in Fig. 1. Fig. 3 represents curves made from densitometer records taken along the lengths of the lines. With each of these lines there is an arc line which gives the posi-

tion of the electron beam. All the lines were obtained on one plate at a single exposure. The pressure of helium in the tube was 1.2×10^{-2} mm of Hg, the electron voltage was 500 volts and the transverse electric field was 305 volts/cm, while the magnetic field was 2520 gauss. The electron current collected to 6 was 0.5 milliamperes and the positive ion current to electrode 3 was 0.025 milliampere.

The shape of the electron beam in this case was so irregular that it was impossible to obtain values for the average life, but it sufficed for the purpose of comparing the average lives for the different lines. From Fig. 3 we see that for the lines 4686A (4→3) and 3203A (5→3) the displacements in the direction of motion of the helium ions are small. However, the line 2733A (6→3) shows clearly a displacement in the direction in which the positive ions are moving. The next line of this series 2511A, (7→3) exhibits a greater shift than the previous line 2733A. From Eq. (7) we see that the lines which

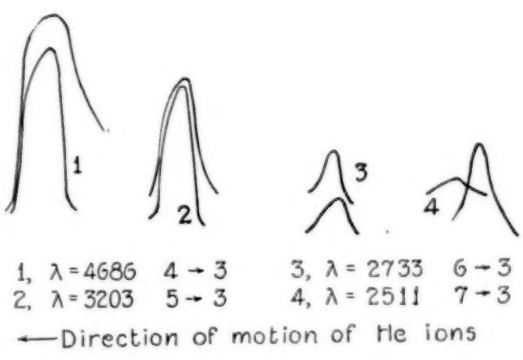

Fig. 3. Experimental results obtained illustrating the relative displacements of the first four lines of the "4686" series of He^+.

have the greatest displacements must originate from levels which have the longest mean lives. *Therefore, these experimental results show that the average life becomes progressively greater for levels with larger total quantum numbers.* This is in agreement with the theoretical values for the average life as shown in Table I.

Simultaneous ionization and excitation by electron impact.

In the derivation of the intensity formulas, it was assumed that at the time of collision the atom is ionized and excited. Compton and Boyce[12] have shown that the spark lines of helium can be formed only by single electron impacts when the electron current densities and gas pressures are low. This was proven by the fact that electrons with 65 volts energy excited only the arc lines of helium whereas the spark spectrum was fully developed at 85 volts. The spark spectrum would have appeared at 55 volts if it had been caused by cumulative action. This has been later confirmed by Elenbass[13]

[12] Compton and Boyce, Jour. Frank. Inst. **205,** 497 (1928). See also Compton and Lilly, Astrophys. J. **52,** 1 (1920).

[13] Elenbass, Zeits. f. Physik **59,** 289 (1930).

who found that the 4686A line of ionized helium did not appear until about 80 volts.

It was found in the present experiment that with the cross field applied, the line 2733A became very weak as the voltage was decreased until at about 80 volts it remained only strong enough to be measured. In order more accurately to determine the initial potential for the appearance of this line, the transverse electric field was removed so that the electron velooities would be more uniform. It was found that the line was entirely absent at 65 volts whereas it was visible at 82 volts. This confirms the results obtained by the above workers.

We see from the previous work that the intensity of the displaced spark line at any given position along its length is proportional to the electron cur-

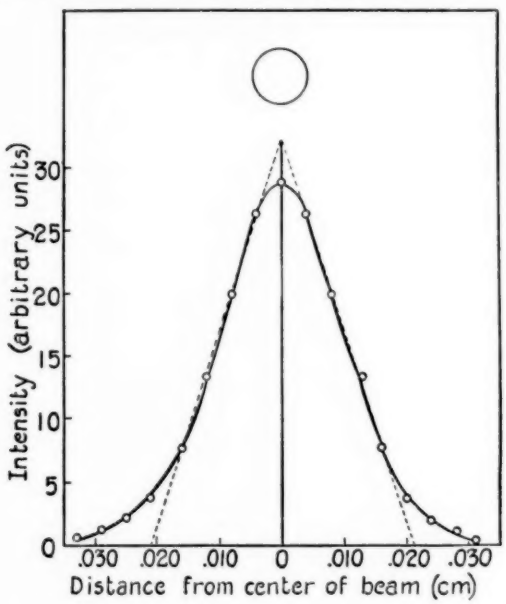

Fig. 4. Intensity distribution of line 2733A without the transverse field. The circle represents the cross section of the filament drawn to scale illustrating the size of the beam in comparison with the diameter of the filament.

rent if the excitation is produced at a single collision, whereas if it is due to a double collision the intensity will be proportional to the square of the electron current. Measurements of the relative intensity of both the 4686A and 2733A lines have been made as a function of the electron current with the transverse field applied and the intensity was found always to be directly proportional to the electron current showing therefore again, that the excitation occurs at a single collision.

Shape of the electron beam.

In the derivation of the intensity formulas it was assumed that the intensity of the electrons in the beam increased uniformly up to the center of the beam and then decreased uniformly to the upper edge of the beam. Fig. 4 shows how the intensity of the line 2733A varies along its length for the case of

no transverse field. This illustrates that the distribution of electrons is nearly the same as the assumed distribution. The dotted lines forming a triangle represent the distribution of electrons which give a width of the beam equal to 0.041 cm. The circle in the upper part of the figure represents the cross section of the 7 mil diameter tungsten filament drawn to scale with respect to the rest of the figure.

When the electric field is applied this distribution is not appreciably changed as long as the velocity of the exciting electrons is greater than the minimum speed for ionization and excitation. This fact is demonstrated by measuring the intensity distribution of a suitable arc line of helium. A line must be selected which is not lengthened by absorption and reemission of the light in leaving the tube. This line must also be excited by approximately the same speed electrons which are capable of ionizing and exciting the helium atom. The helium arc line 4437A was selected because for the case of no transverse field it had practically the same distribution of intensity as the helium spark lines. When the field was applied the shape of the line indicated that the distribution in intensity was practically unaltered for the beam used here. The assumption of the distribution of intensity for the subsequent calculation of the mean life is thereby justified.

Average life for sixth quantum state.

Fig. 5 shows enlargements made from the actual negatives obtained with the experimental arrangement as given in Fig. 1. Negatives are reproduced here for cases with and without the transverse electric field. The line 2733A of ionized helium is drawn up in the direction of motion of the positive ions when

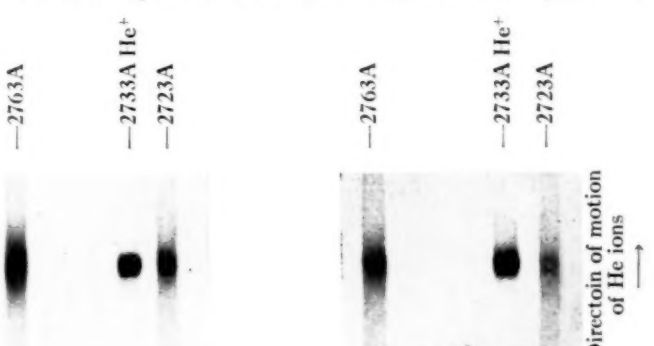

Fig. 5. Enlargements (magnification, five times) made from original negatives obtained for (1) without transverse field and (2) without transverse field showing effect of motion of helium ions for line 2733A. The adjoining arc lines located the center of the electron beam.

the field is applied. The lines 2763A and 2723A are two principal series lines of the orthohelium system. They are unaffected by the electric field and their densest portion locates the center of the electron beam. In exposure 2 the electrons had approximately 210 volts velocity, while the cross electric field was 740 volts/cm. The currents and pressure were the same as for the pre-

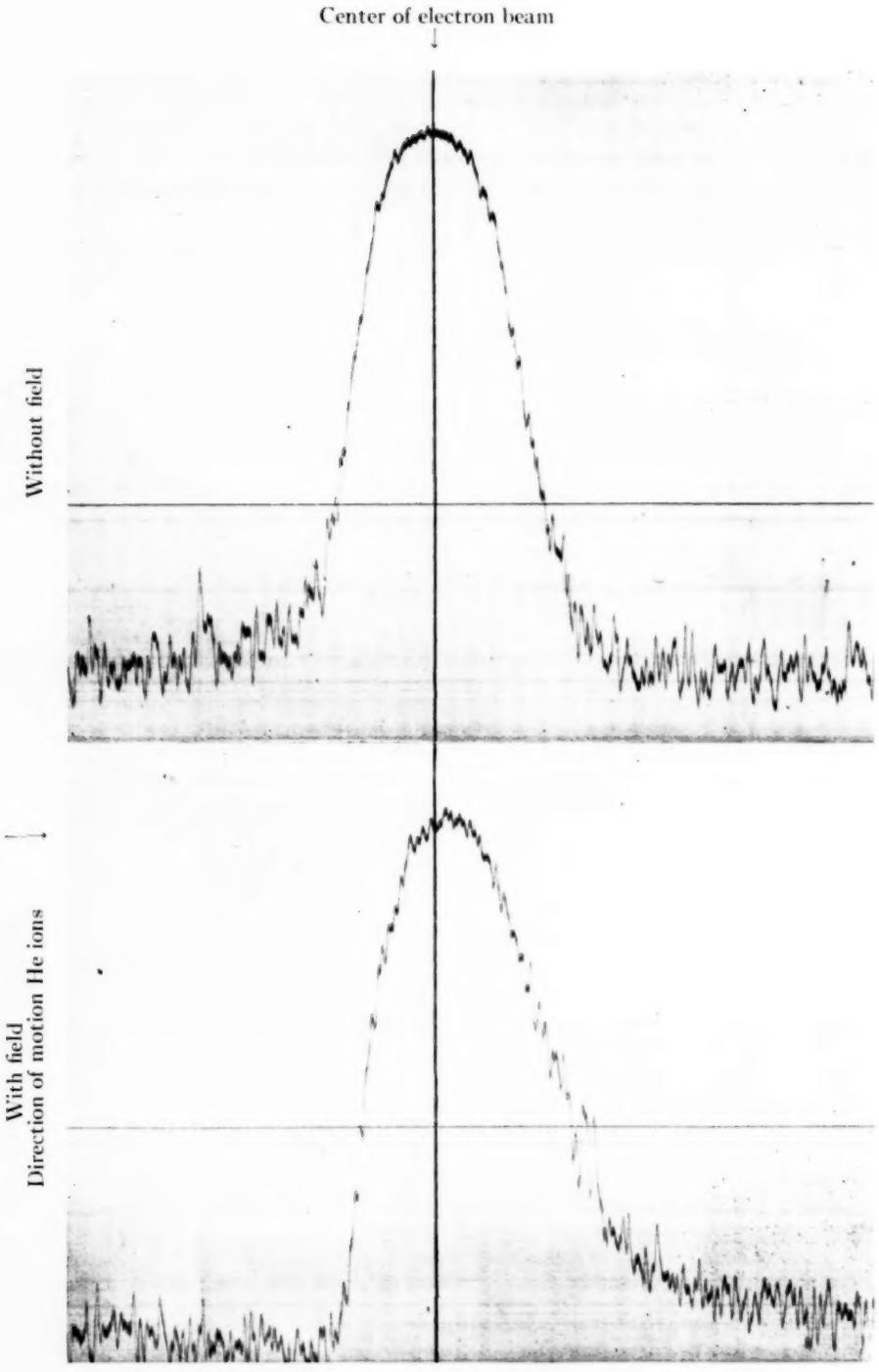

Fig. 6. Microphotometer records of line 2733A for (1) without cross field, and (2) with cross field. Vertical line marks center of electron beam located by helium arc lines 2723A and 2763A.

vious experiment described above. The magnetic field was 2520 gauss. The spectrum was photographed on an Eastman speedway plate with an exposure of twelve hours. The experimental conditions for exposure 1 were similar to 2 except that the cross field was zero and the voltage of the electrons was 350 volts.

Fig. 6 shows two records made by a Goos and Koch microphotometer taken along the length of the line 2733A, (1) with and (2) without the transverse electric field. The vertical line locates the center of the beam as determined by the center of the two adjoining arc lines shown in Fig. 5. This is accomplished by making microphotometer records for these two arc lines which lie on opposite sides of the line 2733A. By this means it is possible to correct for error produced by improper alignment of the direction of motion of the spectrum plate in the microphotometer. From Fig. 6 we see that for record (2) the line is displaced in the direction of motion of the helium ions. Record (1) is made from the plate shown in exposure 1 of Fig. 5. (2) is taken from an exposure in which the accelerating potential was about 120 volts, the cross field 650 volts/cm, the other conditions were the same as given above.

In Table III are given the experimental values obtained for the average life determined for different energies of the exciting electrons. *It is seen that*

TABLE III.

Energy of electrons in beam (volts)	Average life experimental values for sixth quantum state (sec.)	Mean average life theoretical value sixth quantum state
260	$1.6\pm0.2\times10^{-8}$	
120	$1.5\pm0.2\times10^{-8}$	
112	$1.3\pm0.2\times10^{-8}$	
100	$1.1\pm0.2\times10^{-8}$	
80	$1.1\pm0.2\times10^{-8}$	1.17×10^{-8} sec.

the experimental values for the average life decrease as the energy of the electrons is diminished, and approaches the theoretical value for the mean average life. As the energy of the exciting electrons is decreased there will be less excitation to the levels higher than the sixth. The number of transitions downward into the sixth state will thus decrease and cause the average life to become shorter. This conclusion is substantiated by the fact that as the voltage is lowered the intensity of the line 2511A coming from the seventh state diminishes faster than does the intensity of the line 2733A coming from the sixth state. Thus the ratio of the number of electrons in the sixth state to the number in the seventh becomes greater as the voltage is decreased. This will produce fewer transitions into the sixth state and consequently the average life of the sixth state will become shorter. Because of the small energy differences between the sixth and seventh levels it is practically impossible to excite to the sixth state with enough intensity to produce lines which can be photographed, while at the same time produce no excitations to the seventh state.

The values obtained at 100 volts and 80 volts differ from the theoretical value for the mean average life by less than 0.10×10^{-8} sec. which is consider-

ably less than the experimental error. The agreement obtained here is better than is found by other workers for the case of hydrogen. For example, the theoretical values for the mean average life of the 2nd, 3rd, and 4th quantum states of hydrogen are 2.18×10^{-9} sec., 1.03×10^{-8} sec. and 3.4×10^{-8} sec. respectively. Wien's[14] canal-ray measurements on H_α of the Lyman series give 6.7×10^{-9} sec. for the average life of the second quantum state. Slack[15] obtains experimentally the value of 1.2×10^{-8} sec. for this state. For the third quantum state Wien again obtains 6.7×10^{-9} sec. from measurements on H_b of the Lyman series while Wien and Kerschbaum[14] obtain 1.85×10^{-8} sec. from H_α of the Balmer series. Their results for the fourth state as determined by H_β give the same value of 1.85×10^{-8} sec.

Curve 1 in Fig. 7 gives the intensity distribution of the line 2733A with respect to the center of the beam, while curve 2 represented by the dotted line gives the theroretical intensity distribution calculated by the use of the

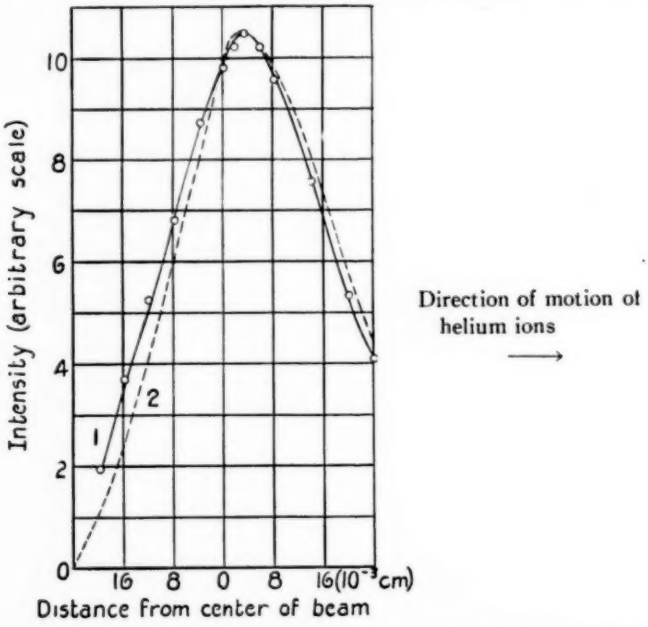

Fig. 7. Intensity distribution of line 2733A found experimentally, given by curve 1 while curve 2 shows a similar distribution calculated from intensity formulas using the theoretical value for mean average life.

intensity formulas (7) and (8)[16] for the average life of 1.17×10^{-8} sec., the value given in Table III for the mean average life. The two curves show approximately the same distribution of intensity, which gives an agreement between the experiment and the theory. It is noticed that the width of the beam is 0.048 cm as compared to 0.041 cm as is given in Fig. 4. This slight increase

[14] Wien, Ann. d. Physik **83,** 1 (1927); See also table of values for average lives from canal ray experiments of Wien and Kerschbaum, prepared by Kerschbaum, Ann. d. Physik **83,** 294 (1927).

[15] Slack, Phys. Rev. **28,** 1 (1926).

[16] These numbers refer to equations on page 725, Phys. Rev. **32,** (1928).

in the width of the beam is probably caused by the action of the transverse electric field.

In order to compare the average life measured experimentally with the theoretical value for the mean average life, there must be a continuous interchange between the sublevels so that the number of electrons in any sublevel is proportional to its quantum weight. Sugiura has pointed out in connection with the interpretation of Wien's canal-ray experiments, that the perturba-

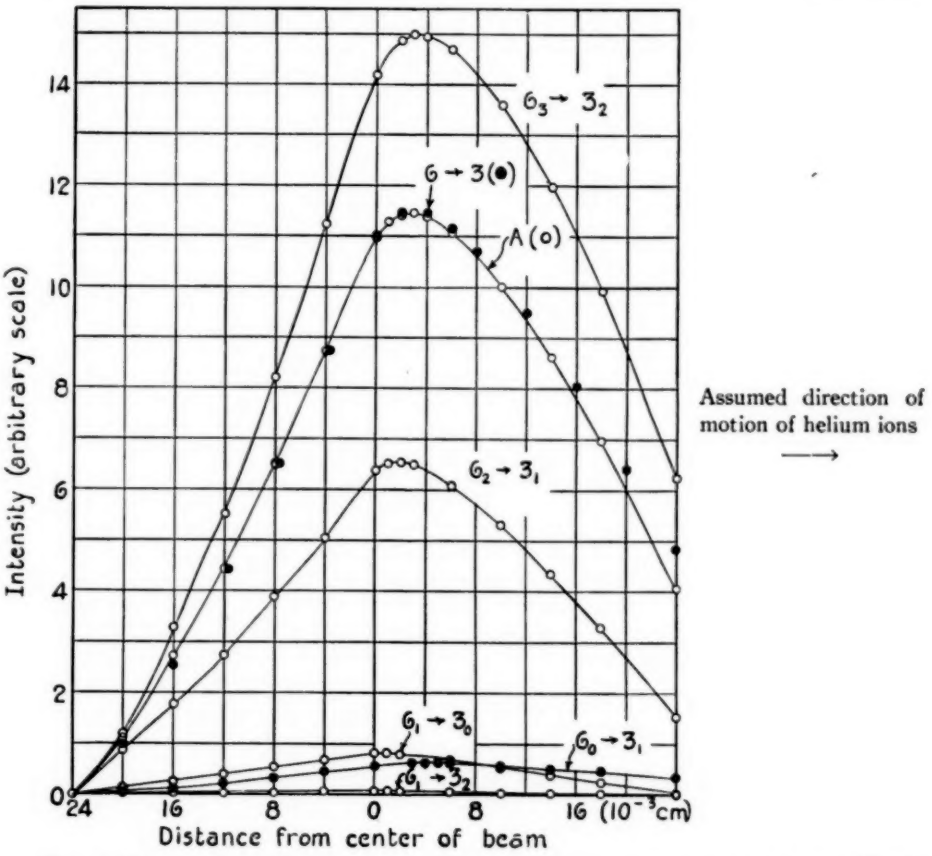

Fig. 8. Theoretical intensity distribution for the five fine structure lines of the line 2733A. Curve *A* represented by the circles is the resultant intensity curve plotted on a reduced scale. Curve 6→3 indicated by full dots gives the intensity distribution for the case of free interchange among the *l* values (or for the case of a single exponential decay law). The values for the average life used were taken from Table I, and 658 volts/cm was the strength of field used.

tions to which the hydrogen atoms were subjected were large compared with the component separations due to relativity, so that free interchange existed among the various sub-divisions of a term. In the present work the helium ions radiate in the presence of crossed electric and magnetic fields which further complicates the perturbations of the quantum states. However Elenbass[17] has found that the line 4686A of ionized helium is polarized when ex-

[17] Reference 13.

cited by unidirectional electrons. To interpret these results one must assume that free-interchange did not take place, otherwise the light could not be polarized.

In the present work we cannot prove the existence of statistical equilibrium so that it is considered a postulate for comparing the results of experiments with the mean average life.

Alternative interpretation of the experimental results.

It is, however, possible to obtain a comparison with the theory by considering the decay time of each of the fine structure lines which make up the single line 2733A, without the assumption of statistical equilibrium. A theoretical intensity curve is obtained for each line individually and then a resultant intensity curve is plotted and compared with the theoretical intensity curve obtained above for the case of free interchange. This method requires a knowledge of the relative population of the substates at the time of excitation.

The results of these computations are illustrated in Fig. 8. The theoretical intensity distribution for the five fine structure lines is plotted with respect to the distance from the center of the beam. The relative intensities of these curves for a given position depends upon the transition probability $A_{n,l}^{n',l}$ the quantum weight g_l, and the average life $1/\beta(n,l)$ as given in the formulas for the intensity distribution.[18] It is noticed that the two lines $6_3 \rightarrow 3_2$ and $6_2 \rightarrow 3_1$ predominate and determine approximately the intensity distribution of the resultant intensity curve A which is plotted on a reduced scale. Thus the curve A represented by the circles gives the theoretical intensity distribution for the case of *no interchange* between the l values. There is also plotted in this figure the values of the intensity for the case of *free interchange* or (in other words for the case of a single exponential decay law), taken from curve 2 in Fig. 7 and is represented by $6 \rightarrow 3$ located by the full dots. It is seen that these two sets of points lie almost identically on the same curve which shows that the theoretical distribution is the same for the two cases. Thus we have shown that we cannot distinguish between the two methods of interpreting the experimental results. Both are in good agreement with the experimental intensity distribution obtained.

If we take into account electron spin correction we find that each of the above five lines split up into groups of lines. Since we have proved above that the average life of the n,l,j,th state is equal to the average life of the n,l,th state, therefore, these lines resulting from spin will have the same average life as the line from which they originated. This means that in this case we shall have five groups of lines with average lives corresponding to the average lives of the five lines given above. Also the sum of the intensity of the lines in any particular group is proportional to the intensity of the parent relativistic line independent of l.[19] Therefore, the relative intensity of the sum of the intensities of the lines in a group will be the same as the relative inten-

[18] The values for $A_{n,l}^{n,l'}$ and the average life used here are obtained from Slack's table although Kupper's values could be used without greatly changing the results obtained.

[19] This has been proved above. See also Sommerfeld and Unsöld, Zeits. f. Physik **38,** 237 (1926).

sity of the five single lines for the relativistic case. Thus we see that the *distribution of intensity of the resultant line calculated by considering all the additional fine-structure lines due to spin will be exactly the same as for the relativistic case.*

Errors

(1) Approximate solution.

The most fundamental error is caused by the fact that the shape of the electron beam is never actually the ideal case in which the distribution is triangular as assumed in the calculation of the intensity of the displaced lines. A more exact treatment could be obtained by a numerical integration performed by introducing experimental values for the electron distribution func-

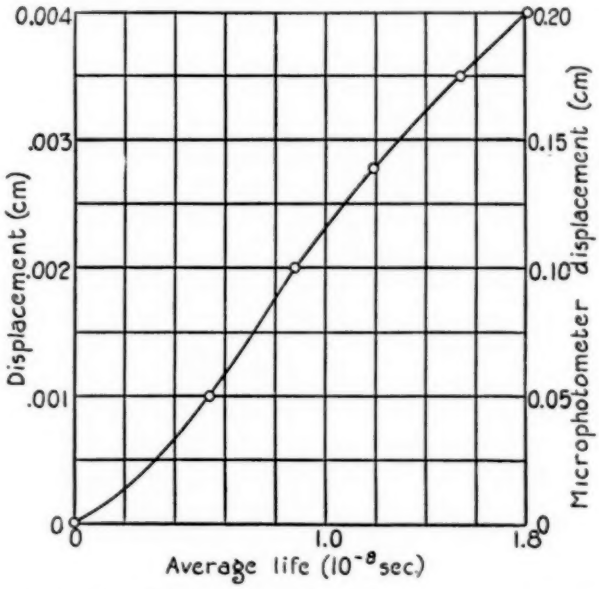

Fig. 9. Relationship between the displacements and the average life for a field of 658 volts/cm, and beam width 0.048 cm.

tion $N(\xi)$. However, Fig. 4 shows that the distribution obtained is approximately triangular so that the results are sufficiently accurate to compare satisfactorily with the theory.

(2) Center and shape of the electron beam.

In the present experimental conditions there exists a cross field of approximately 660 volts/cm. Since the width of the beam is approximately 0.04 cm there is a drop of potential of about 26 volts across the electron beam itself. This means that there will be a distribution of velocities across the beam within this amount. This will alter the effective distribution curve and will be more pronounced in the case where the speed of the exciting electrons is only a small amount in excess of the minimum velocity required for excitation. This error will become practically negligible for higher velocities of the order of 150 volts or more. It is very difficult to determine the amount of this

error for the lower velocities without knowing the probability of excitation function for both the arc lines and the spark lines.

(3) Measurements of displacements.

Fig. 9 shows the relationship between the average life and the displacement of the maximum of the shifted spark line for a cross field of 658 volts/cm. On the ordinate axis there is plotted at the left of the figure the displacements, while at the right is plotted the corresponding distances which are actually measured on the microphotometer record. On the abscissae is plotted the average life for a beam of width 0.048 cm. These are the constants used in obtaining the results given in Table III. The error in reading the displacements on the microphotometer record was not greater than 0.2 mm. Therefore we see from Fig. 9 that the corresponding error for the average life is 0.20×10^{-8} sec. This is the error given in Table III.

(4) Effect of the thermal velocities of the helium ions.

In the above calculations of the average life it is assumed that when the excited ion is formed it is initially at rest. This, of course, is never actually the case on account of the thermal velocities possessed by the ions. A helium atom or ion at a temperature of 20°C has a root mean square velocity of 1.38×10^{5} cm/sec. Under the action of a transverse electric field of 732 volt/cm the ion, initially at rest, would obtain this velocity of 1.38×10^{5} cm/sec. after being accelerated through a distance of 5.33×10^{-5} cm. This distance is small compared to the distances considered in the present experiment. Thus the initial velocity due to thermal agitation of the ion can be neglected.

(5) Space charge.

To reduce the effect of space charge in these experiments, the electron current in the beam was decreased until it required about 12 hours exposure to photograph the line 2733A. The electron currents in the beam were not greater than 0.5 milliampere and the positive ion current was less than 0.06 milliampere. *It was found that the displacements of the spark line 2733A were not appreciably altered when the currents were reduced to about one-half the above values.* This indicates that the distribution of space charge in the presence of the strong transverse field does not disturb appreciably the velocities of the helium ions.

(6) Shape of emitting portion of the filament.

Although the displacements measured are of the order of 0.002 cm it is unnecessary for the filament to be straight and in proper alignment to less than this amount. The filament however, was not actually straight for its central portion sagged about 0.002 cm. This part of the filament would be out of alignment with the other portions by an amount comparable to the experimentally measured displacements. However, the intensity photographed by the spectrograph is the resultant of the radiation coming from different depths of the beam. Although each radiating segment is not in alignment with the optic axis of the spectrograph and the projecting lens, nevertheless the displacement recorded by the photographic plate will be

exactly the same as if the segments were in very accurate alignment. This is true provided that all segments radiate with the same intensity, which is practically the case. Therefore, any sagging or improper alignment of the filament will produce no error in the measured displacements, but it will obviously produce an error in the value for the width of the beam and in the intensity distribution curves. These errors of 0.002 cm are so small that they are unimportant in determining the width of the beam, however they became more important in the measurement of the intensity distribution.

(7) Vibrations of the filament.

The maximum amplitude of vibration of the filament due to the interaction between the alternating heating current and the magnetic field was about 0.001 cm which is small compared to the width of the beam so that it caused no appreciable errors.

In conclusion the writer desires to express his thanks to Dr. A. Bramley for helpful discussions of the work.

Note added in proof, October 2, 1931:

In view of the discrepancies given above for the matrix amplitude squared, Professor Slack has recalculated his values for the intensities and transition probabilities for hydrogen and has kindly furnished the data for Table IV.

With Slack's corrected values for the transition probabilities we find that the average life of the 5_0, 6_0, 7_0, 7_3 and 7_4 states are changed to 2.2×10^{-8}

TABLE IV. *Summary of corrected intensities in the 4th, 5th, and 6th series of hydrogen* (Prepared by Slack).

Component	Previously published* Intensity ergs/sec.	Previously published* Probability sec.$^{-1}$	Corrected Intensity ergs/sec.	Corrected Probability sec.$^{-1}$	Matrix amplitude squared	Kupper's matrix amplitude squared
5_4-4_3	20.8×10^{-7}	43.0×10^{5}	20.8×10^{-7}	43.0×10^{5}	628	630
5_3-4_2	12.6	26.1	12.6	26.1	297	291
5_2-4_1	7.26	15.0	7.26	15.0	122	125
5_2-4_3	0.246	0.507	0.246	0.507	4.13	4.4
5_1-4_0	3.60	7.43	3.60	7.43	36.3	36
5_1-4_2	0.0092	0.019	0.92	1.9	9.3	9.1
5_0-4_1	6.09	12.54	3.15	6.49	10.58	105
6_4-4_3	9.94×10^{-7}	13.3×10^{5}	9.94×10^{-7}	13.3×10^{5}	53.3	55
6_3-4_2	9.85	13.2	9.85	13.2	41.1	40
6_2-4_1	6.58	8.81	6.58	8.81	19.6	22.5
6_2-4_3	0.094	0.126	0.161	0.215	0.48	0.48
6_1-4_0	3.88	5.19	3.88	5.19	6.88	6.0
6_1-4_2	0.0075	0.010	0.75	1.0	1.30	1.21
6_0-4_1	3.11	4.16	2.44	3.25	1.45	14.8
7_4-4_3	7.94×10^{-7}	8.75×10^{5}	3.97×10^{-7}	4.37×10^{5}	14.6	14.7
7_3-4_2	8.65	9.55	4.57	5.04	12.9	12.9
7_2-4_1	4.28	4.73	4.28	4.73	8.6	6.7
7_2-4_3	0.057	0.063	0.057	0.063	0.115	0.137
7_1-4_0	2.38	2.63	2.38	2.63	2.88	2.15
7_1-4_2	0.0041	0.0045	0.41	0.45	0.49	0.41
7_0-4_1	1.98	2.19	1.77	1.95	0.71	4.2

* Slack, reference 4.

TABLE IV. (*continued*)

Component	Previously published Intensity ergs/sec.	Previously published Probability sec.$^{-1}$	Corrected Intensity ergs/sec.	Corrected Probability sec.$^{-1}$	Matrix amplitude squared	Kupper's matrix amplitude squared
6_5-5_4	4.20×10^{-7}	16.0×10^{5}	4.33×10^{-7}	16.4×10^{5}	1852.	201.
6_4-5_3	2.63	10.0	2.63	10.0	921.	1020.
6_3-5_2	1.97	7.50	1.97	7.50	538.	520.
6_3-5_4	0.045	0.17	0.030	0.114	8.15	8.2
6_2-5_1	1.14	4.32	1.14	4.32	226.	203.
6_2-5_3	—	—	0.078	0.295	15.1	20.
6_1-5_0	0.617	2.35	0.617	2.35	72.3	67.
6_1-5_2	—	—	0.268	1.02	31.3	15.3
6_0-5_1	1.97	7.50	0.69	2.63	26.9	247.
7_5-5_4	2.40×10^{-7}	5.69×10^{5}	2.40×10^{-7}	5.69×10^{5}	154.	139.
7_4-5_3	2.46	5.82	2.46	5.82	128.	122.
7_3-5_2	1.97	4.66	1.97	4.66	80.	75.
7_3-5_4	0.0093	0.022	0.20	0.48	0.82	0.81
7_2-5_1	1.27	3.01	1.27	3.01	37.	36.
7_2-5_3	—	—	0.808	1.91	2.35	2.37
7_1-5_0	1.01	2.40	1.01	2.40	17.6	20.7
7_1-5_2	—	—	0.258	0.66	4.8	3.9
7_0-5_1	1.10	2.60	0.583	1.38	3.4	35.
7_6-6_5	1.13×10^{-7}	7.10×10^{5}	1.20×10^{-7}	7.5×10^{5}	4500.	4497.
7_5-6_4	0.635	4.00	0.635	4.0	2020.	2734.
7_4-6_3	0.617	3.89	0.545	3.43	1420.	1582.
7_4-6_5	0.0113	0.071	0.0057	0.036	15.0	14.1
7_3-6_2	0.421	2.65	0.421	2.65	850.	848.
7_3-6_4	—	—	0.016	0.10	32.4	36.3
7_2-6_1	0.235	1.48	0.246	1.55	356.	
7_2-6_3	—	—	0.030	0.19	43.7	58.9
7_1-6_0	0.051	0.32	0.159	1.0	138.	
7_1-6_2	—	—	0.098	0.62	85.	
7_0-6_1	1.04	6.53	0.20	1.26	58.	

sec., 3.3×10^{-8} sec., 5.0×10^{-8} sec., 2.4×10^{-8} sec., and 4.5×10^{-8} sec., respectively. The values for the average life of the other states and the mean average lives remain practically the same. The only lines illustrated in Fig. 8 affected by these corrections is the transition $6_0\rightarrow3_1$. Since this component is weak in comparison with the other transitions, the resultant intensity curve *A* is not appreciably changed.

MASS SPECTROGRAPH ANALYSES, AND CRITICAL POTENTIALS FOR THE PRODUCTION OF IONS BY ELECTRON IMPACT, IN NITROGEN AND CARBON MONOXIDE

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(Received August 11, 1931)

Abstract

The dissociation products formed by bombarding nitrogen and carbon monoxide with electrons of a definite velocity have been studied with a mass spectrograph.

Nitrogen.—N_2^+ and N^+ ions appear at 15.8 ± 0.1 and 24.5 ± 0.1 volts respectively. The N^+ ion has kinetic energy and is attributed to $N_2 \rightarrow N^+ + N + e$. Increases in the efficiency of production of the N^+ ion appear at 40.0 ± 1.0 and 47.0 ± 1.0 volts. The largest percentage of the total positive ion current carried by kinetic energy ions is approximately 28 percent at 140–160 volts. Efficiency curves of total ionization and of N_2^+ exhibit maxima at 100.0 ± 5.0 and 60.0 ± 5.0 volts respectively.

Carbon monoxide.—CO^+, C^+ and CO^{++} ions appear at 13.9 ± 0.2, 22.5 ± 0.2, and 43.0 ± 1.0 volts respectively. Maximum numbers of CO^+, C^+, and CO^{++} ions formed per electron per cm path per mm pressure at 0°C are 10.13, 0.50, and 0.14 at 102, 105, and 125 volts respectively. The C^+ ion possesses kinetic energy and is probably due to $CO \rightarrow C^+ + O + e$. Assuming that the CO^{++} ion would dissociate into $C^{++} + O$ the energy of dissociation cannot be less than from 2 to 3 volts. O^- ions are formed between 9.5 ± 1.0 and 16.5 ± 1.0 volts, and again beginning at 22.5 ± 1.0 volts and reach a maximum at 33 volts. The first group is evidently due to the attachment of an electron to the CO molecule followed by a dissociation $CO^- \rightarrow C + O^-$. The second group may be due to $CO \rightarrow C^+ + O^-$. O^- ions are only 2.7 percent as numerous as C^+ ions at 30 volts.

Introduction

THE material presented in this paper is an extension of the work done by Bleakney[1] on multiply charged ions produced by electron impact in gases at low pressures. The purpose of this paper is to describe the results of a similar study of the ionization products in the diatomic molecular gases—nitrogen and carbon monoxide. Smyth[2] and Hogness and Lunn[3] have made mass spectrograph analyses of the ions produced in nitrogen by electron impact while Hogness and Harkness[4] have made a similar study of carbon monoxide. The present method confirms some of the results of these previous investigations and presents some new data, particularly in the experiments on carbon monoxide.

[1] W. Bleakney, Phys. Rev. **34**, 157 (1929); **35**, 139 (1930); **35**, 1180 (1930); **36**, 1303 (1930)
[2] H. D. Smyth, Proc. Roy. Soc. **104A**, 121 (1923).
[3] T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 786 (1925).
[4] T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 936 (1928).

Apparatus and Procedure

The apparatus employed in this experiment was the same as that used by Bleakney[1] in the study of helium, neon, and argon. The nitrogen and carbon monoxide used were prepared by Smith.[5] The gases were admitted to the apparatus through a fine capillary at the end of the tube opposite the electron gun and were pumped through the ionization chamber and out past the filament. Effects of dissociation by the filament were thus reduced to a minimum. The pressures used were from 5 to 10×10^{-5} mm Hg. The gases used were found to be very pure. Water vapor and a trace of carbon monoxide existed as impurities in the tube before the gas to be studied was admitted. If liquid oxygen were kept on the mercury trap continuously for about 80 hours the water vapor impurity was so reduced as not to interfere appreciably. The carbon monoxide impurity was never large enough to be troublesome except in determining ionization potentials.

Results

Nitrogen

A typical e/m analysis curve of the products obtained by bombarding nitrogen with electrons of definite velocity is shown in Fig. 1. The positive ion current to the analyzer is plotted as a function of the analyzing field, E, in

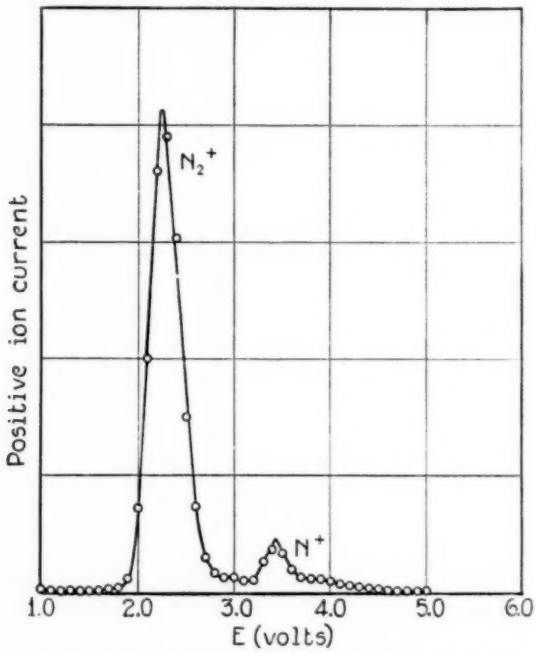

Fig. 1. A typical e/m analysis curve of nitrogen. Electron velocity = 100 volts.

volts. This curve shows the N_2^+ and the N^+ ions. A background of H_2O^+ shows between the two peaks. The trailing off to the right of the N^+ ion may be attributed to those N^+ ions which have considerable kinetic energy.

[5] John T. Tate and P. T. Smith, unpublished.

The ionization potentials of the N_2^+ and N^+ ions were determined by plotting the maximum heights of the peaks as a function of the electron velocity

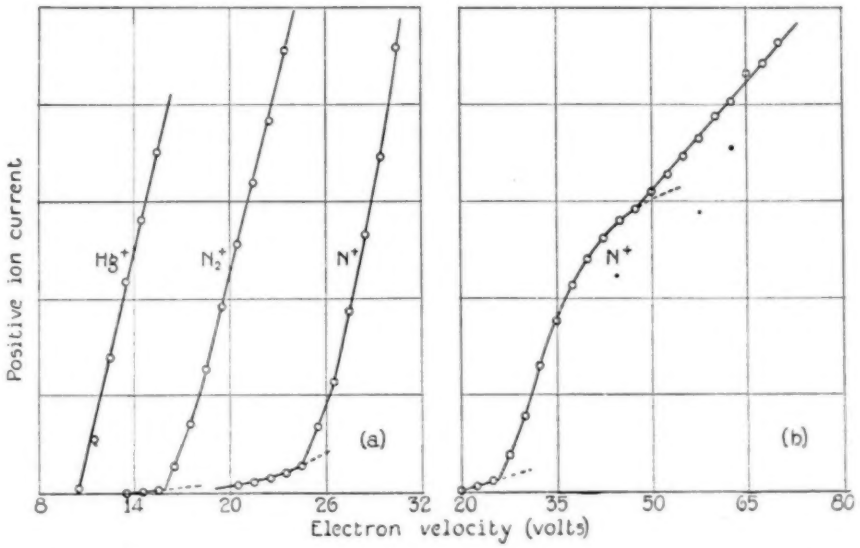

Fig. 2. (a) Curves showing the ionization potentials in nitrogen. (b) Ionization potential curves of N^+ showing a break at 47 volts.

in volts. When the liquid oxygen on the mercury trap was replaced by solid carbon dioxide there was a sufficient amount of mercury vapor present in the

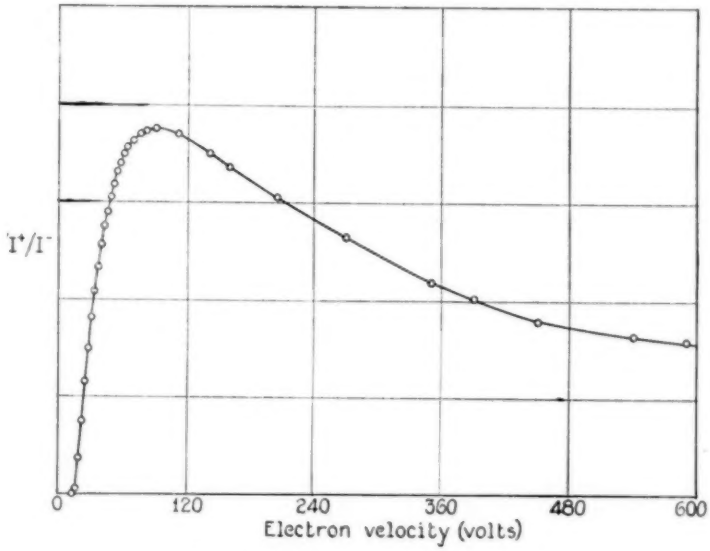

Fig. 3. Efficiency curve for nitrogen.

tube for calibration purposes. The results are shown in Fig. 2 (a). The impurity under the curve for N_2^+ is CO^+ whereas that under the N^+ curve is

H_2O^+. This method shows N_2^+ and N^+ appearing at an electron velocity of 15.8 and 24.5 volts respectively with an estimated probable error of ± 0.1 volts. Fig. 2 (b) shows an increase in the efficiency of production of the N^+ ion at 47.0 ± 1.0 volts. A similar but considerably smaller increase was noticed at 40.0 ± 1.0 volts. These breaks have also been found by Lozier.[6]

By plotting the ratios of the areas under the N_2^+ peak to the electron current as a function of the electron velocity in volts the maximum efficiency of formation of the N_2^+ ion was found to occur at an electron velocity of 60.0 ± 5.0 volts. The total efficiency of ionization as plotted in Fig. 3 shows a maximum at 100.0 ± 5.0 volts. This curve was obtained by plotting the ratio of the total positive ion current collected at the upper plate of the ionization chamber to the electron current as a function of the electron velocity in volts. The efficiency curve of total ionization in N_2 given in Fig. 3 is almost identical with the one obtained by Smith.[5]

A rough measure of the percentage of the current carried by those ions possessing kinetic energy was obtained by the method outlined by Bleakney,[7] and was shown to reach a maximum of 28 percent at 140–160 volts electron velocity. The assumptions made in obtaining this result make it impossible to consider it as other than an indication of the order of magnitude.

Discussion of results in nitrogen.

The value given in this paper of 15.8 ± 0.1 volts as the ionization potential of N_2, although lower than the generally accepted value, agrees with that given by Samson and Turner[8] and the earlier results obtained by Boucher[9] and by Found.[10] The appearance of N^+ at 24.5 ± 0.1 volts has been attributed to a single impact resulting in $N_2 \rightarrow N^+ + N + e$. The value given is in good agreement with that of 24.6 volts given by Hogness and Lunn[3] who, however, attributed the formation to a different process. According to data given by Samson and Turner[8] together with a correction by Birge[11] the minimum value at which N^+ can appear from the above process is 22.7 ± 0.1 volts. From this the N^+ ion should have at least 0.9 volts kinetic energy. These conclusions have been verified by Lozier.[6] There was no means of determining whether or not any N_2^{++} ions were formed since their m/e is the same as that of the N^+ ion. No N^{++} ions were found below 400 volts. No search was made for negative ions.

Carbon monoxide

Fig. 4 is a typcial e/m analysis curve of the positive ions formed by bombarding CO with electrons. Ions having an m/e of 28, 14, and 12 were found which correspond to CO^+, CO^{++}, and C^+ and have ionization potentials of 13.9 ± 0.2, 43 ± 1.0, and 22.5 ± 0.2 volts respectively as obtained from Fig. 5.

[6] W. W. Lozier, unpublished.
[7] W. Bleakney, Phys. Rev. **35,** 1185 (1930).
[8] L. A. Turner and E. W. Samson, Phys. Rev. **34,** 747 (1929).
[9] P. E. Boucher, Phys. Rev. **19,** 189 (1922).
[10] C. G. Found, Phys. Rev. **16,** 41 (1920).
[11] R. T. Birge, Phys. Rev. **34,** 1062 (1929).

The second peak from the left in Fig. 4 is due to an ion having an m/e of 18 and an ionization potential of 13.2 volts and so has been attributed to H_2O^+. Solid carbon dioxide instead of liquid oxygen was used on the mercury trap in this experiment. The O^+ ion, if formed, was entirely masked by the H_2O^+ ion.

The two e/m analysis curves in Fig. 4 were taken at electron velocities of 35 and 210 volts. They show the resolving power of the apparatus as well as the relative magnitudes of the ions formed at those velocities. Attention is called to the complete absence of an ion having an m/e of 14 at 35 volts electron velocity. The determination of the ionization potential of CO may not be accurate since the positive ion current due to the Hg^+ ion which was used

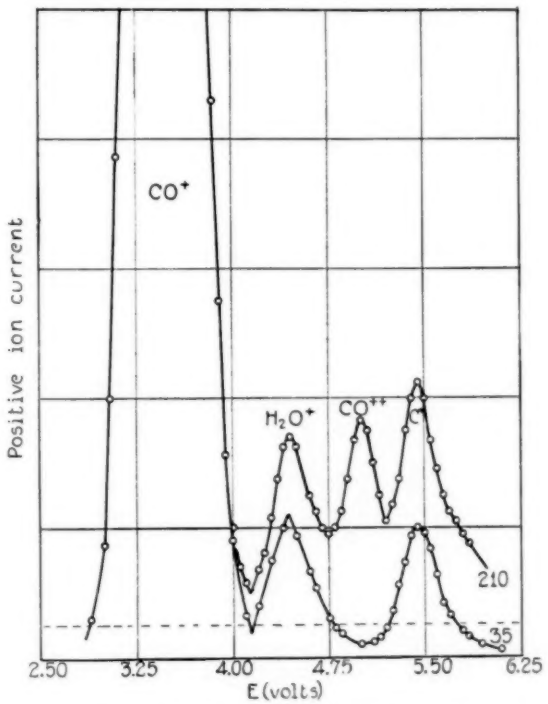

Fig. 4. e/m analysis curves of carbon monoxide taken at electron velocities of 35 and 210 volts.

to calibrate the voltage scale was very small compared to the positive ion current due to the CO^+ ion. The impurity shown under the C^+ curve in Fig. 5 was H_2O^+ while that under the CO^{++} was C^+ and H_2O^+. It was found that by decreasing the drawing out field in the ionization chamber the C^+ peak shown in Fig. 4 decreased considerably in size. This was an indication that the C^+ ion was formed with kinetic energy. This also afforded a means whereby more accurate measurements could be made of the CO^{++} ion inasmuch as decreasing the size of the C^+ peak made the CO^{++} peak stand out more distinctly. An increase in the efficiency of formation of the C^+ ion was consistently evident at about 30 volts.

Fig. 6 shows the percent of positive ion current carried by the different

ions. These curves were obtained by plotting the ratios of the areas under the peaks to the electron current as a function of the volt velocity of the impinging electrons. Multiplying the total number of ions formed as given by Smith[5] by the percent of current carried by a particular ion and dividing by the

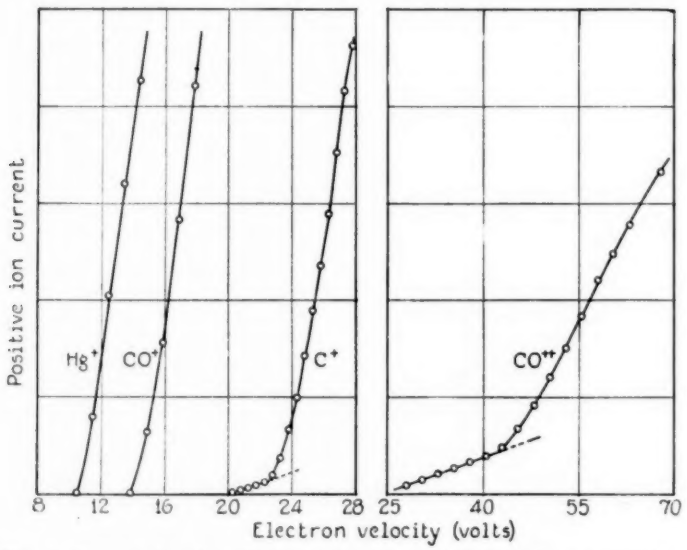

Fig. 5. Curves showing the ionization potentials in carbon monoxide.

charge on the ion gives the number of that type of ion formed per electron per cm path reduced to 1 mm pressure at 0°C. These results are shown in Fig. 7. The numbers of CO^+, C^+, and CO^{++} ions formed reach maxima of 10.13, 0.50, and 0.14 at 102, 105, and 125 volts respectively. An independent determina-

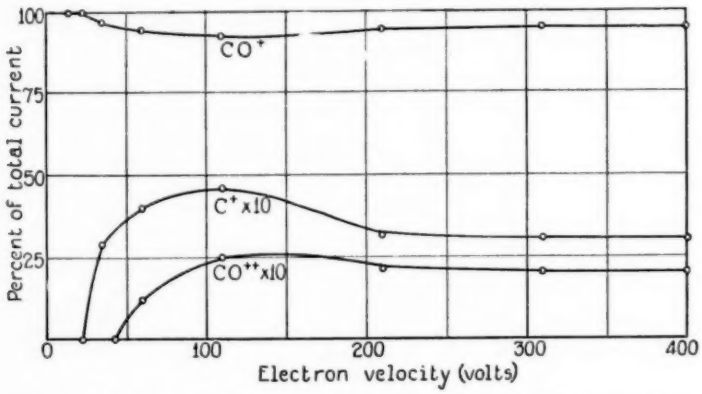

Fig. 6. Percent of total positive ion current carried by CO^+, C^+, and CO^{++} ions.

tion of the efficiency of formation of the CO^+ ion obtained by plotting the area under the peak yielded a maximum at 100 volts.

Negative ions having an m/e of 16 were found in carbon monoxide. These negative ions which are undoubtedly O^- first appeared at 9.5 volts, reached a

sharp maximum at 12 volts and had completely disappeared at 16.5 volts as shown in Fig. 8. The same type of negative ions reappeared at 22.5 volts

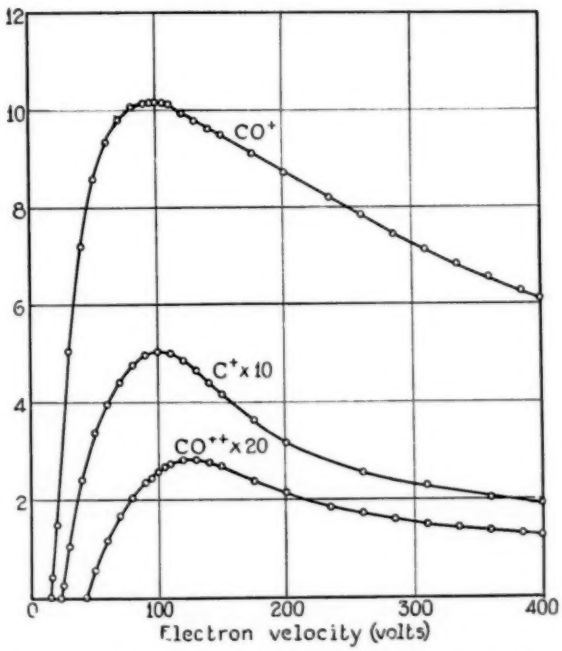

Fig. 7. Number of ions, N, formed per electron per cm path per mm pressure at 0°C.

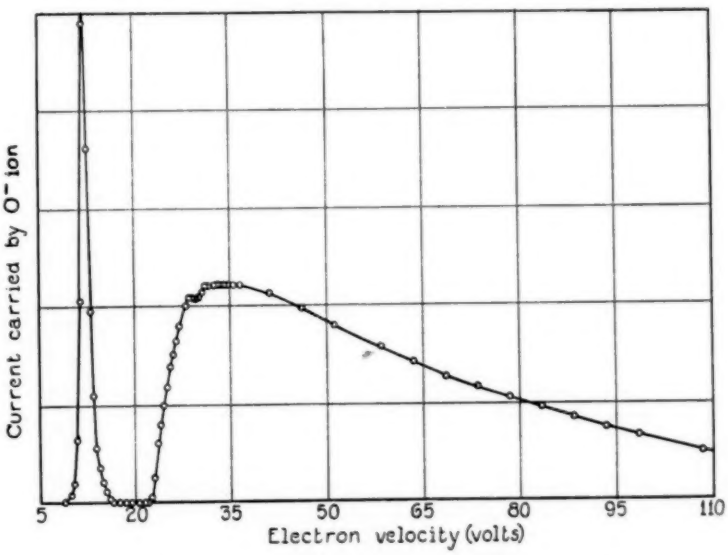

Fig. 8. Current carried by O^- ion in carbon monoxide.

and increased to a maximum at 33 volts and then dropped off gradually as the electron velocity was increased. These voltages given are accurate only to

within a volt since the correction had to be calculated rather than determined experimentally. Fig. 8 was obtained by plotting the maximum height of the O^- peak in the analyzer as a function of the electron velocity. If the O^- ion formed at 9.5 – 16.5 volts has no kinetic energy and if the one starting in at 22.5 volts does have kinetic energy then the relative heights of the two parts of the curve are not accurate. In this case the second part would be too small. The dip in the curve at 29 volts appeared consistently. This break was also detected by another method[6] in this laboratory. It may be that this dip is associated with the break found at 30 volts in the C^+ ionization potential curve. The O^- ion was found to be only 2.7 percent as numerous as the C^+ ion at an electron velocity of 30 volts.

Discussion of results in carbon monoxide.

The value of 13.9 ± 0.2 volts as given in this paper as the ionization potential of CO agrees with that given by Hogness and Harkness[4] but may be in error as mentioned before. Birge[12] gives a calculated value of 14.2 volts. In a private communication Mulliken gives the most probable value of the heat of dissociation of CO as 9.8 volts. With the value given by Hopfield[13] of 11.2 volts as the ionization potential of the carbon atom the minimum electron velocity at which the C^+ ion could appear by the single process $CO \rightarrow C^+ + O + e$ is 21 volts. The appearance of C^+ at 22.5 ± 0.2 volts indicates 1.5 volts kinetic energy to be divided between the dissociation products. The value of 22.5 ± 0.2 volts is also in good agreement with the value of 22.8 volts given by Hogness and Harkness.[4]

The CO^{++} ion appearing at 43.0 ± 1.0 volts is, so far as the author knows, the first multiply charged polyatomic molecule whose ionization potential has been determined. J. J. Thomson[14] found a doubly charged molecular ion having an m/e of 28 and attributed it to either N_2^{++} or CO^{++}. R. Conrad[15] has identified several doubly charged molecules in the glow discharge of mixtures of methane, oxygen, and water vapor.

The experimental value of 43.0 ± 1.0 volts for the critical potential of $CO \rightarrow CO^{++} + 2e$ indicates that the dissociation products of the doubly charged ion are most likely to be $C^{++} + O$ rather than $C^+ + O^+$ or $C + O^{++}$. If one combines the energy necessary to dissociate CO into C+O which is 9.8 volts as given above with the ionization potentials of 11.2[12] and 13.5[16] volts for atomic carbon and oxygen respectively 34.5 volts is obtained for an assumed dissociation of CO into $C^+ + O^+$. As this is much less than the observed value of 43 volts it does not seem possible that $C^+ + O^+$ can be the correct dissociation products. In a similar way with the 35[17] volts energy necessary to remove the second electron from atomic oxygen one gets 58.3 volts

[12] R. T. Birge, Nature **117**, 229 (1926).
[13] J. J. Hopfield, Phys. Rev. **35**, 1586 (1930).
[14] J. J. Thomson, "Rays of Positive Electricity," 2nd Ed., p. 84 (1921).
[15] R. Conrad, Phys. Zeits. **31**, 888 (1930).
[16] J. J. Hopfield, Astrophys. J. **59**, 114 (1924).
[17] R. A. Millikan and I. S. Bowen, Proc. Nat. Acad. Sci. **13**, 531 (1927).

for the energy necessary to dissociate CO into $C+O^{++}$. Since it seems unlikely that the dissociation energy of CO^{++} can be as high as $58.3-43\backsimeq 15$ volts, and since in the formation of CO^{+} the dissociation products were found to be $C^{+}+O$ and not $C+O^{+}$, the dissociation of CO^{++} into $C+O^{++}$ is very improbable. The dissociation into $C^{++}+O$ requires 9.8 $(CO\rightarrow C+O)+11.2(C+O\rightarrow C^{+}+O+e)$[12] $+24.3(C^{+}+O\rightarrow C^{++}+O+e)$[17] $=45.3$ volts which shows that the heat of dissociation of the CO^{++} ion cannot be less than from 2 to 3 volts.

The only thing to be said about the O^{-} ion at the present time is that its first appearance is probably due to an attachment of an electron to a CO molecule followed by the dissociation $CO^{-}\rightarrow C+O^{-}$. The fact that it appears only over a small range of electron velocities lends support to the above interpretation. The second appearance may be due to a splitting up of $CO\rightarrow C^{+}+O^{-}$. The negative ion will be discussed by Lozier.[6]

It is a pleasure to acknowledge the constant interest and timely suggestions of Professor John T. Tate and the many helpful discussions with Drs. W. W. Lozier and P. T. Smith.

THE EMISSION OF NEGATIVE IONS UNDER THE BOMBARDMENT OF POSITIVE IONS

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(Received September 11, 1931)

Abstract

The results which Sawyer obtained from the reflection of lithium ions from reflectors of platinum foil and nickel crystal deposited on tungsten, indicated two distinct angles at which reflection occurs more strongly than at other angles, one coming nearly at the angle of specular reflection as found by Read and Gurney, and the other which appeared only at relatively high voltages, at an angle approximately normal to the reflecting surface. Experiments made by reflecting the lithium ions from a metal surface in a field free space gave the bundle at the specular angle as before, but no trace of a bundle at the normal to the surface could be found. When a field is applied so as to retard reflected positive ions there was evidence of negative emission coming from the target under the bombardment of lithium ions. A magnetic analysis system was set up to determine the nature of the negative charges. Negative fluorine, chlorine, oxygen and sulphur ions were obtained by bombarding NaF, CaF_2; NaCl, CaO, PbS and oxide-coated vacuum tube filaments. Clean metal targets of platinum, gold, aluminum, tantalum, nickel, and tungsten were found to emit electrons and the negative ions H_1^-, H_2^-, OH^-, and Cl^- with traces of what is probably N^- and $LiOH^-$. The strongest bundles were the first four which indicate that water-vapor molecules were broken up into their components.

Introduction

THE results which Sawyer[1] obtained from the reflection of lithium ions reflected from reflectors of platinum foil and nickel crystals deposited on tungsten, indicated two distinct angles at which reflection occurs more strongly than at other angles, one coming nearly at the angle of specular reflection as observed by Read[2] and Gurney[3] and the other, which appeared only at relatively high voltages, at an angle approximately normal to the surface of the reflector. This latter beam was observed when the reflection took place in strong electrostatic field. The present investigation developed out of a further study of this normally reflected beam. It was suspected from these experiments that the observations were complicated by a new type of emission, namely the emission of negative ions from metal surfaces under the bombardment of positive ions. The second part of the paper describes a direct investigation of this new phenomenon and gives an analysis, by the methods used for positive rays, of the types of negative ions obtained in this way.

Part I

The tube used in the first experiments on reflection of positive ions by metals was the one described by Sawyer modified somewhat as shown in Fig.

[1] R. B. Sawyer, Phys. Rev. **35,** 1090 (1930).
[2] G. E. Read, Phys. Rev. **31,** 629 (1928).
[3] R. W. Gurney, Phys. Rev. **32,** 467 (1928).

1. In this a strip of platinum foil *F* carrying a small crystal of spodumene on a constricted portion served as a source of positive ions when heated electrically. After heating to a yellow heat for several minutes the emission is practically all lithium ions. These ions are drawn to the drum *D* by a potential applied from the outside of the tube. The collector *C* was a small Faraday chamber subtending an angle of about 9 degrees from the target *T*. It was supported by a stiff wire insulated from the rest of the apparatus. Connection to the electrometer was made through very flexible nickel ribbon wound like a clock spring. The whole collector system was very carefully shielded from any possible ions escaping from the filament by enclosing the collector in a hood, and by a disk which covered the end of the cylinder *H* and extended beyond the guard ring *G*. The collector and cylinder were rotated on a common axis by means of an electromagnet applied from the outside to the arm-

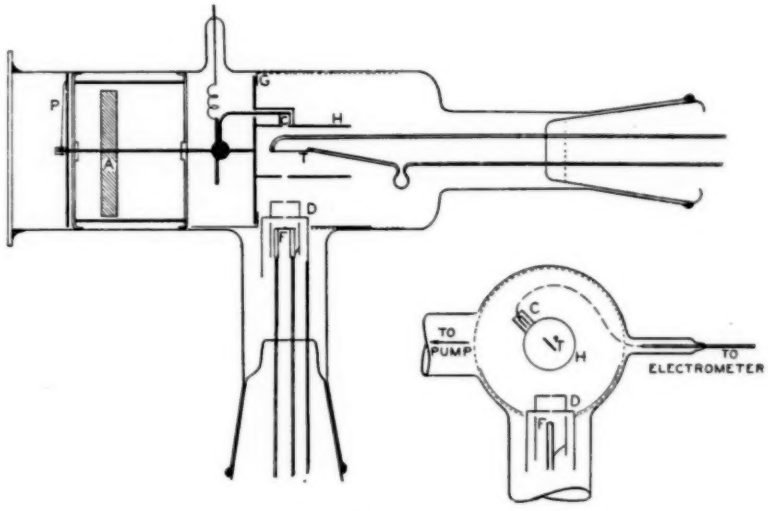


Fig. 1.

ature *A*. The angle reading could be made through the Pyrex window with the pointer *P* on the scale.

The target *T* on which the lithium ions fell, was a strip of platinum foil about 0.3 cm wide and 1 cm long. It was held in place by two leads, one of which was flattened and bent to serve as a spring to keep the target taut. The other was placed behind the target to reduce field distortion. A piece of nickel gauze was put over the slit in the cylinder *H* in the region of the collector in order to reduce the distortion of the field.

As the target and filament had to be changed frequently two ground joints were used, that were sealed by a ring of picein cement about the outer edge. No difficulty was experienced with contamination of the target, as it was kept at a low red heat throughout the observations.

To examine the reflection in its simplest form the ions were allowed to strike the target in a field free space. This was done by applying an accelerating potential between the filament and drum, and the retarding potential be-

tween the cylinder and collector. When the positive ions were reflected in a field free space the peak at the angle corresponding to specular reflection appeared as before, but no trace of a peak at the normal could be found. This was true in the apparatus used by Sawyer, and also in the modified form which differed only in the use of a Faraday chamber as a collector, which was shielded in front by a nickel gauze in order to avoid all electric fields in the reflecting chamber. In the case of Sawyer's experiments the potential was applied partly between the filament F and the drum D and partly between the cylinder H and target T, the drum and cylinder being at the same potential. The cylinder to target potential served as an accelerating voltage for the incident ions, and at the same time as a retarding potential for the same ions after reflection.

It was also found that when the gauze was put over the slot in the cylinder, and a retarding field for positive ions was applied between the target and cylinder, there was evidence of negative charges coming to the collector when it was nearly normal to the target. In one instance a negative potential of 28 volts had to be applied to the collector to prevent it from collecting negative charges which are then presumably deflected into the gauze. Since the specular bundle remained positive as before, it is reasonable to assume that the negative ions were formed on the target and accelerated to the cylinder by the field that retarded the reflected positive ions.

To compare the sharpness in angle of a beam of ions liberated at the target with the negative beam actually observed, a bit of spodumene was put on the target and heated. With no accelerating voltage some of the positive ions found their way to the collector, but with a few volts accelerating potential a very narrow intense beam was observed. This indicates that the field at the surface of the target is normal to it and is strong enough to form a beam strongly concentrated in the normal direction.

Attempts to eliminate the negative charges, obtained by bombardment of the target, by putting an electromagnet around the tube in such a way as to deflect them away from the collector were unsucessful. The nickel shields may have weakened the magnetic fields to a certain extent but the insensitiveness of the negative charges points to the emission being ionic rather than electronic in nature.

Although we may explain the negative charges observed near the normal to the target as due to secondary negative ions set free by bombarding positive ions, the reflected positive ion bundle which Sawyer observed is more difficult to explain. Since the beam occurs only when the field is strong inside the cylinder the concentration of the ions at the normal is probably due to the field itself. It may be that, since the target is wide in comparison to the diameter of the cylinder, the lines of force are in such a direction that ions reflected from the center of the target would be reflected specularly, while those striking the target nearer the edges would be drawn toward the normal, after reflection, by the field.

PART II

To identify the negative charges freed from a metal surface by positive ion bombardment and to see whether they are electrons or ions a Dempster[4] magnetic analysis system was set up as shown in Figs. 2 and 3. A filament *F* coated with spodumene was made positive with respect to the target *T* supported above it. Any negative ions formed at the target would be accelerated downward by this same potential. Some of them would go by the edge of the filament and pass through the slit *S* into the magnetic field. With a stream of ions of the same mass and the same velocity a value of the magnetic field

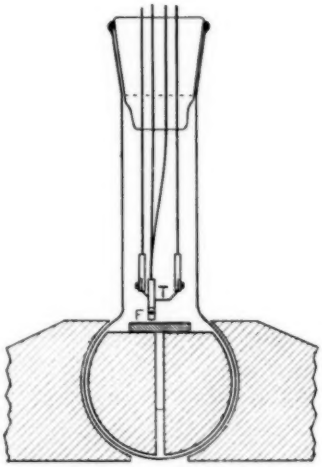


Fig. 2.

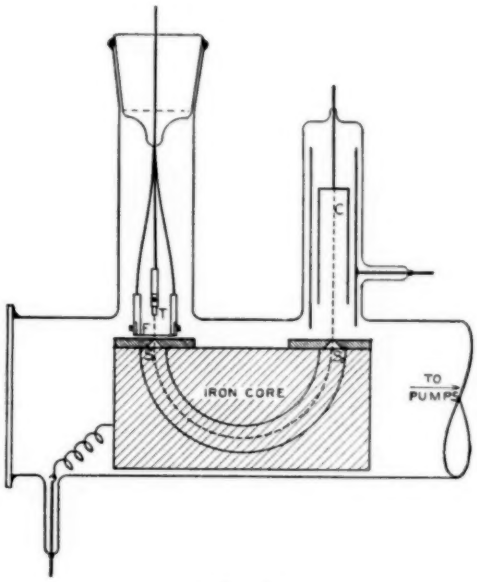


Fig. 3.

could be found that would deflect them through a semi-circle and allow them to pass out through the other slit *S* to the collector *C*.

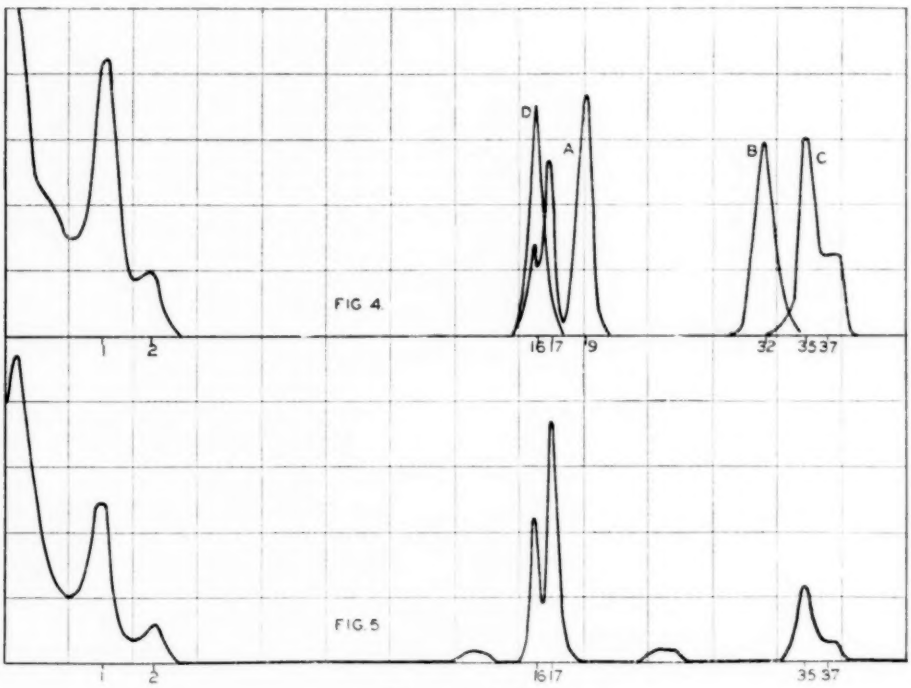
The first results with the apparatus gave a considerable negative ion emission, but the resolution was not good enough to separate definite ion bundles. At this time the experiments were interrupted, but Dr. J. S. Thompson kindly undertook to carry out the analysis of the ions. He introduced some improvements in the apparatus, such as the shield about the collector, which greatly improved the resolving power. With the improved apparatus he was able to demonstrate the emission of negative ions and to identify several distinct negative ion bundles.[5]

Experiments were later resumed by the author with the same apparatus to study further the different kinds of ions that may be obtained in this way. To avoid uncertanty in identifying the ions the slits were narrowed to 0.8 mm and the apparatus calibrated by means of positive ions that were accelerated

[4] A. J. Dempster, Phil. Mag. **7** Series 13, 115 (1926).
[5] J. S. Thompson, Phys. Rev. **38,** 1389 (1931).

at various potentials. When heated, spodumene liberates positive ions of lithium, and traces of sodium, and potassium according to other investigators[6] and these ions are brought to the collector successively as the field strength in the iron armature is increased. Assuming the magnetic field to be symmetrical when the magnetizing current is reversed, the mass of the negative ions may be deduced. Later the calibration was checked by the use of negative fluorine ions.

Richardson[7] finds that negative ions are obtained from iodides, chlorides, bromides, and fluorides by heating their salts. Barton[8] found negative ions of mass 33 to be liberated from the oxides of strontiun and barium when heated.



Figs. 4 and 5.

This suggested that electronegative ions might be obtained from the bombardment of their salts by positive ions. The negative ions obtained by bombarding various salts are shown in Fig. 4. The ion intensity is plotted against the magnetizing current. Fig. 4A shows the negative ions obtained by bombarding NaF or CaF_2 with 500 volt lithium ions. The ion at 19 does not appear at all when the platinum target is clean, but appears with great intensity when the target is covered with the fused fluoride salt, thus definitely associating the peak with the negative fluorine ion. The method of applying consists of wetting the surface of the target with a solution of the salt. As the target is

[6] J. L. Hundley, Phys. Rev. **30,** 864 (1926).
[7] O. W. Richardson, Emission of Electricity from Hot Bodies, p. 107.
[8] H. A. Barton, Phys. Rev. **26,** 360 (1930).

slowly heated the water evaporates leaving a fine layer of salt on the target, which can be fused by further heating. CaF_2 could not be dissolved in water but was powdered and the powder dusted on the target with a bit of cotton, then fused by heating. A thick film is undesirable as there may be considerable voltage drop through it. No negative ion emission was obtained by simply heating the target, that was strong enough to observe by the methods used in these experiments.

The ions obtained by bombardment of NaCl fused to the target are shown in Fig. 4C. Considerable intensity was obtained when the target was cold, but in common with other salts, the emission was stronger when it was heated. The ions show the doubling to be expected from the isotopic nature of chlorine and the agreement with 35 and 37 is very good. No chlorine ions were observed when the bombarding ion current was cut off and the target heated only. The method of applying this salt to the target by evaporating a solution of it on the target surface does not work out well in this case, since the salt crystals explode when they lose their water of crystalization. A small hood held over the target effectively holds the escaping crystals until they have been fused. Richardson[7] found that negative ions were obtained by heating manganous chloride that had molecular weights between 59 and 88, showing that the ions were of atomic or molecular magnitude and possibly molecular chlorine. Barton[9] found a few negative chlorine ions from HCl formed either by bombardment with low velocity electrons or from thermal dissociation at a hot filament.

In Richardson's experiments there are no records of negative ions of the elements in the sixth column of the periodic table. Barton[8] thought his ion of mass 33, which was obtained from heating barium and strontium oxides, might be due to molecular oxygen. He found no negative atomic oxygen however as might have been expected. The question as to whether negative atomic oxygen is freed from its compounds under positive ion bombardment was investigated by depositing calcium oxide on a platinum target. On bombarding it with lithium ions the negative ion bundle shown in Fig. 4D was obtained. It could be identified definitely from the calibration curve as having a mass 16. Although molecular oxygen (32) was looked for, no trace of it could be found. The impacting ion evidently frees atomic oxygen which is drawn to the collector before it has a chance to combine with another atom to form a molecule.

When a commercial oxide-coated vacuum tube filament was used as a target, negative ions of atomic oxygen gave a strong peak when the filament was bombarded with lithium ions. Before it had been heated it gave in addition a more intense bundle at mass 17, but this disappeared when the target was heated, leaving only the peak at 16. The oxide coated strip was then activated by heating to a yellow heat for several minutes an applying a potential until a strong emission of electrons was obtained. The negative ion emission from it, by bombardment, then gave the two peaks at 16 and 17 in the same pro-

[9] H. A. Barton, Phys. Rev. **30**, 614 (1927).

portions as before it had been heated. This indicates that moisture remains in the oxide coated filaments even after they have been heated to a bright yellow heat and "activated" by drawing electrons from them for some time.

The emission of negative oxygen ions from oxides, by bombardment, suggested that sulphur ions might be obtained from sulphides. PbS was powdered and fused to a clean platinum target, great care being taken not to decompose the substance. When bombarded with the positive lithium ions no effect was produced until the target was heated, then the peak shown in Fig. 4B appeared with a mass 32. No negative ions are emitted when the bombarding ion current is cut off even through the target is hot. Schmidt[10] finds no ions up to a temperature of 450°C by the heating of PbS. We conclude then that the bombardment of lithium ions dissociates the hot sulphide and frees negative ions of sulphur.

When ever any of the substances examined were bombarded with positive ions we get in addition to their characteristic ion bundles several distinct peaks as shown in Fig. 4 to the left. The peak nearest the axis is due to electrons and varied in intensity somewhat. The peak at mass 1 was very strong and a much weaker peak appeared at mass 2. These are evidently H_1^- and H_2^- that have been knocked out by the impinging positive ions, probably from water vapor contained in the salts.

From the negative ions, produced as described above, a calibration of the magnet was made which checked approximately with the positive ion calibration, but showed that the magnetic field was not absolutely symmetrical on reversal.

In addition to the clean platinum target used by Thompson targets of aluminum, gold, tantalum, nickel and tungsten were bombarded with positive ions. The negative ion beams emitted by these various metals resemble each other closely, indicating that the emission is independent of the metal of the target. A typical negative ion "spectrum" is shown in Fig. 5. The strong emission near the axis occurs at a field too weak to deflect anything more massive than electrons. The most prominent peaks occur at exactly 16 and 17 and are unquestionably due to O^-, and OH^-. Another strong bundle occurs at mass 1, with a much weaker one at mass 2. Since these two are probably H_1^- and H_2^- and they occur with O_1^- and OH^- in such large quantities in all metals observed, it appears that the lithium ions must strike water vapor molecules on the surface of the target, breaking them up into their components which are drawn to the collector. The fact that the H_1^- and OH^- bundles are stronger than the H_2^- and O^- bundles seems to support such an hypothesis.

The next strongest negative ion beam comes at 35 and 37 and is unquestionably chlorine since the position and shape of the curve is exactly the same as that obtained when the target is coated with NaCl. Just as any fresh metal will give the characteristic yellow color of sodium when first put in a Bunsen flame, so these negatively charged chlorine atoms appear to be present in all

[10] G. C. Schmidt, Ann. d. Physik 75, 337 (1924).

metals tested. Prolonged bombardment however makes them disappear. The smaller peaks at 13 and 24 to 25 are much less intense. They do not occur at all in metals that are exceedingly pure and have clean surfaces. After the metal has been bombarded for some time they disappear. Probably they are N_1^- and $LiOH^-$.

The negative ions produced by bombardment of metal surfaces are evidently due to contamination of the target or to adsorbed gases. Cl^-, O_1^- and OH^- ions nearly all disappear from targets such as platinum and tungsten when they are heated to a bright yellow heat for five minutes or more. In distinction to this behavior the emission of ions from oxides, chlorides, fluorides and sulphides persists as long as the salt remains on the target.

In the experiments described above the potential between the target and the filament was 500 volts. An attempt was made to find a critical voltage below which the negative ions were not freed from the target by bombardment, but no critical lower potential could be observed. The intensity of the negative ion beam decreased rapidly as the voltage was reduced, but some negative ions were observed as low as 50 volts.

In conclusion the writer wishes to acknowledge his indebtedness and express his appreciation to Professor A. J. Dempster who proposed the problem and whose suggestions for its development have been invaluable. The writer also wishes to thank Dr. R. B. Sawyer and Dr. J. S. Thompson for their cooperation and valuable assistance.

THE RESIDUAL IONIZATION IN NITROGEN AT HIGH PRESSURES

By James W. Broxon
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(Received September 22, 1931)

Abstract

The residual ionization in nitrogen at high pressures was measured under conditions existing during a recent investigation of the residual ionization in air, with lead and water shields. As in earlier investigations, the residual ionization in nitrogen was found to be greater than that in air at all pressures. However, at the new high pressures the ionization-pressure curve becomes parallel to the pressure axis, as do the air curves. The explanation in terms of subsidiary radiations excited by the cosmic penetrating radiation in the walls of the ionization chamber serves as well for nitrogen as for air. The new work is discussed in relation to earlier investigations of the residual ionization in air, oxygen, nitrogen and carbon dioxide.

RECENTLY the writer[1] investigated the ionization produced by the cosmic penetrating radiation in aged, dry air contained in a large spherical ionization chamber at pressures up to 170 atmospheres. Earlier investigations[2] of the residual ionization in four gases, air, oxygen, nitrogen and carbon dioxide, over a pressure range extending from 1 to 70 or 80 atmospheres, had shown that within this range the ionization in the former two gases was very nearly the same under corresponding conditions. The latter two gases also yielded nearly identical ionization values, but in these gases the absolute values of the ionization and also the final slopes of the ionization-pressure curves were decidedly greater than in the cases of air and oxygen. Further, the forms of the ionization-pressure curves obtained with nitrogen and carbon dioxide were such as to arouse a suspicion that constant slopes of appreciable magnitude might have been attained. In view of these observations and the essentially constant values of the residual ionization in air measured at the higher pressures in the more recent work, it appeared that a special investigation of the residual ionization in nitrogen at the new high pressures would be of value.

Equipment and Procedure

The nitrogen used was obtained from a commercial concern. It would seem that in the process of purification of the nitrogen by evaporation from liquid air, any radium emanation would be retained in the oxygen and the nitrogen would be particularly free from radioactive contamination. However, in view of the high ionization values formerly observed, the nitrogen was kept stored in cylinders for a period of six months before being admitted into the chamber in which the ionization was measured.

[1] J. W. Broxon, Phys. Rev. **37**, 1320 (1931).
[2] H. F. Fruth, Phys. Rev. **22**, 109 (1923); J. W. Broxon, Phys. Rev. **27**, 542 (1926).

According to a statement by the company manufacturing it, the nitrogen was 99.8 percent pure, with 0.2 percent argon and oxygen. The gas was passed through a long tube containing phosphorus pentoxide and also plugs of glass wool and cotton to remove moisture and dust, precisely as in the case of the high pressure measurements in air. The chamber was washed by admitting and then releasing the gas until, as calculated on the basis of fractional removal, less than 10^{-6} percent of the gas finally investigated should have consisted of air originally in the ionization chamber. However, the gas as it was released from the ionization chamber was analyzed by Mr. K. A. Gagos of the University Department of Chemistry, and was found to contain 0.72 percent oxygen, with no observable carbon dioxide or water vapor. No test was made for argon. Mr. Gagos used a Bureau of Mines[3] apparatus, and estimated his accuracy at 0.02 percent. Subsequent analysis of gas obtained directly from the commercial cylinders, incidentally, showed that some of these had an even greater oxygen content.

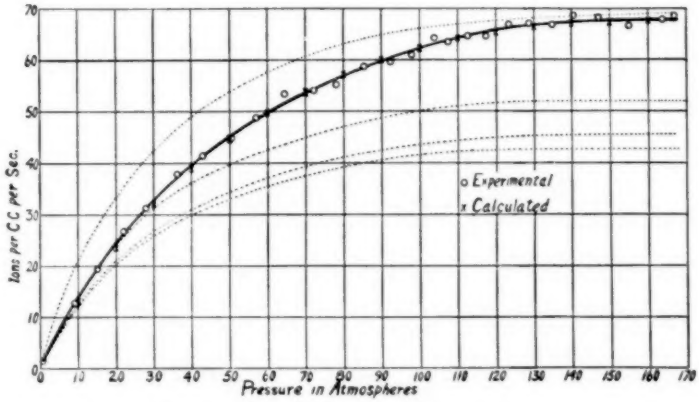

Fig. 1. Residual ionization in nitrogen.

The ionization was measured with precisely the same equipment used in the investigation of air,[1] the location of the apparatus and the method of measurement remaining unchanged. Because of the expense involved, only one series of pressure observations could be made. These were made[4] with the ionization chamber surrounded both by the two-inch lead shield and by the water shield formed by filling the fourteen-foot water tank in the center of which the ionization chamber was located. The series of readings extended over a five-day interval, June 15–19, 1931.

Observations

The observed ionization values are shown plotted against the pressures in Fig. 1. The actual temperatures during the observations varied between 15.35°C and 17.5°C. In order to facilitate comparison with the ionization-pressure curves previously found for air, the pressures were changed to cor-

[3] Bull. Bur. of Mines **42**, 17 (1913)

[4] Measurements of the dielectric constant of the nitrogen at the high pressures were made, also, and will be presented in a later paper.

responding pressures at 18°C, and these are the pressures designated in the diagram. In order further to facilitate comparison, the four curves formerly[1] obtained with air with various conditions as to shielding are represented in the diagram by dotted lines.

Discussion

Notwithstanding the long aging of the nitrogen, the ionization in this gas was again observed to be very considerably higher than that in air under the same conditions. The lowest of the dotted curves represents the ionization in the air under corresponding conditions, with both shields about the ionization chamber. At all pressures at which observations were made, extending from 0.82 to 167 atmospheres, the ionization in the nitrogen was greater than that in the air at corresponding pressures. In fact, the relation between the new high pressure nitrogen and air curves is nearly the same, in the region of the earlier investigation, as the relation between the nitrogen and air curves obtained by the writer[2] at sea level in 1925, these measurements having been made with entirely separate equipment, but with ionization chambers of about the same size and shape. If the ionization in excess of that at atmospheric pressure as observed with the present equipment with both lead and water shields is divided by the corresponding values obtained in the 1925 work with the unlined twelve-inch sphere, the ratio obtained in the case of air increases from 0.29 at 20 atmospheres to 0.30+ at 70 atmospheres, while the corresponding ratio in the case of nitrogen increases from 0.32 to 0.35 in the same region. The ionization in the nitrogen does not appear to have been decreased quite as much as that in air by the heavy shielding, but perhaps this may be accounted for by the fact that the nitrogen used in the earlier investigation was also commercial nitrogen, and no test of its purity was made.

A very significant characteristic of the new nitrogen curve is the very small slope at the high pressure end. Although the ionization at first increases with increase of pressure more rapidly than does that in air, so that the curve approaches that obtained with air with no special shielding, yet the slope continues to decrease with pressure and appears to be quite definitely zero (not exceeding 0.02 or 0.03 ion/cc·sec·atm.) at the high pressure end, precisely as in the case of the curves obtained with air. The region of constant ionization values does not begin at quite as low pressures as do those obtained with air, but it is sufficiently extended to establish definitely the very small value of the final slope. Therefore, on the basis of the explanation of the ionization-pressure relation previously suggested, in terms of secondary radiations excited by the cosmic penetrating radiation in the walls of the container, the ionization measurements made with the two gases now agree in showing an exceedingly small primary ionization due directly to the penetrating radiation. On this basis, however, it would appear that the secondary radiations with nitrogen in the chamber must be somewhat more penetrating and ionize more copiously than in the case of air. The form of the nitrogen curve is better represented by the simple relation derived by the writer[1] in explanation of the observations made in air, than is the case with the air curves. The calculated

values designated in the diagram were obtained by the use of this relation and the assumption that 90 percent of the final maximum ionization was due to radiations of range corresponding to 180 atmospheres in the bomb (roughly 180 diameters of the bomb in nitrogen at atmospheric pressure) and 10 percent to radiations of range corresponding to 50 atmospheres. The final slope of the curve found by differentiating the theoretical expression thus obtained and evaluating the derivative at 170 atmospheres is $dI/dP = 0.003$ ion per cc per sec. per atmosphere.

In the opinion of the writer, the chief discrepancy between the residual ionization measurements in the different gases investigated has been removed by the discovery that at the very high pressures practically no increase of ionization with pressure is observed in either air or nitrogen. The greater absolute values[5] of the ionization in nitrogen are quite striking, however, and deserve consideration. This difference between the magnitudes of the ionization in these gases appears to be well established. As mentioned before, the difference was observed both by Fruth[2] and by the writer in the earlier experiments. Moreover, Fruth separated nitrogen from air and found that the ionization-pressure relation was practically the same as in commercial nitrogen, although the nitrogen he prepared contained 4 percent of oxygen. However, when he mixed nitrogen and oxygen in the proper proportions to form air, he observed the same ionization-pressure relation as in air (and oxygen), with the exception of the sharp breaks and the horizontal portions of the curves which he observed at about 53 atmospheres and which have not been verified by the later experiments. Very recently, Professor A. H. Compton discussed with the writer some unpublished work which he has been carrying on. He, also, has observed the constancy of the residual ionization at high pressures, and that the ionization in nitrogen is greater than that in air.

That the difference in absolute values might be due to a radioactive gas in the nitrogen seems very unlikely in view of the precautions taken. Moreover, that it might be due either to this cause or to a spontaneous disintegration of the nitrogen seems unlikely in view of the forms of the ionization-pressure curves. In such a case the ionization would be expected to increase with the density of the gas. Not only does the ionization in each gas fail to increase beyond a certain amount, but the pressure-rate of divergence between the corresponding curves for nitrogen and air, although nearly constant up to about 70 atmospheres, gradually decreases at higher pressures, and the two curves become practically parallel and horizontal at pressures above 140 atmospheres. If the explanation of observations in terms of subsidiary radia-

[5] An observation contributing to the establishment of the fact that the differences among the curves obtained with different conditions as to shielding in the recent investigation of the residual ionization in air at high pressures were due solely to the differences in shielding, was unintentionally omitted from the report (reference 1) of that investigation. The air remaining in the chamber at atmospheric pressure after a series of observations with a particular shield was kept enclosed until the succeeding shielding had been arranged. In each instance the ionization measured under these circumstances was the same as that measured in the new supply of air at atmospheric pressure at the end of the succeeding series of observations.

tions from the walls of the chamber is accepted, the differences among the residual ionization values in the four gases investigated suggest the possibility of the production, whenever sufficient free oxygen is present, of some surface condition causing an appreciable absorption of the subsidiary radiations.

Although the difference between the final values of the ionization in air and nitrogen is very considerable in comparison with either of these, being 59 percent of the maximum ionization in air, it is perhaps worth remarking that the difference is after all a rather small quantity in view of the high pressures; a little more than 25 ions per cc per sec. at 167 atmospheres, the difference amounts only to about 0.15 ion per cc per sec. per atmosphere. At the local atmospheric pressure, the difference between the ionization values is of the order of 0.1 ion per cc per sec.

Grateful acknowledgment is made of the assistance provided by Professor S. L. Simmering and Mr. C. A. Wagner who carefully compressed a portion of the nitrogen to twice the commercial pressures, and by Mr. Louis Strait and Mr. Raymond Jordan who assisted with the recording of observations.

THE DOPPLER EFFECT IN THE CANAL RAYS IN NEON

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(Received September 21, 1931)

ABSTRACT

The neon spectrum in the ultraviolet between 2500A and 4000A from a canal-ray tube was examined for Doppler effects. Potentials up to 24,000 volts were applied to excite the discharge. Doppler effects were found to be present among the stronger lines in the first and second spark spectra of neon and, with only two exceptions, were absent from the arc spectrum lines. About fifty strong and faint lines showing Doppler effects were observed. The canal-ray stream consists of rapidly moving neon atoms which radiate only when in the ionized state. Neon behaves similarly to argon at high voltages and differs from most gases in that the radiation from the canal rays is almost entirely from atoms in the ionized state.

INTRODUCTION

DOPPLER effects among optical frequencies have been well known to exist in certain lines of the line spectra of various gases since Stark's[1] discovery of the effect in 1905. Dorn,[2] working with neon in 1908 obtained several Doppler effects among the strongest lines in the region of the spectrum between 6000A and 7000A. It was thought of interest to photograph the neon discharge in the ultraviolet to find if Doppler effects exist in the region from 2500A to 4000A, and if possible, to find some correlation among the lines showing the effect.

The observations of Friedersdorff[3] with argon show that with potentials above 36,000 volts only the lines of the blue spectrum show Doppler effects, while below that voltage the lines of the red spectrum show small Doppler effects. The neon spark spectra have recently been discovered[4,5] and analyzed[6] and it is of interest to find out the state of ionization of the luminous neon atoms in the canal-ray beam.

APPARATUS AND PROCEDURE

The essential feature of the apparatus consisted of a discharge tube constructed as shown in Fig. 1. The main tube was of Pyrex glass about fifty centimeters long. The cathode, for which the purest commercial aluminum obtainable was used, was made in the shape of a thin disk perforated by a small hole at the center. The anode, also of aluminum, was in the form of a hol-

[1] J. Stark, Phys. Zeits. **6,** 892 (1905).
[2] E. Dorn, Phys. Zeits. **10,** 614 (1909).
[3] K. Friedersdorff, Ann. d. Physik **47,** 737 (1915).
[4] T. R. Merton, Proc. Roy. Soc. **A89,** 447 (1913).
[5] L. Bloch, E. Bloch, and G. Déjardin, Journal de Physique et le Radium **7,** 129 (1926).
[6] T. L. de Bruin, C. J. Bakker, Zeits. f. Physik **69,** 19 (1931).

low cylinder welded to tungsten for sealing through the Pyrex. The main tube extended about seven centimeters beyond the cathode where it was ground flat to accomodate a fused quartz window for end on exposures. Midway between this end window and the cathode a side tube projected normally two centimeters beyond the main tube. A fused quartz window covered this side tube permitting photographs to be taken of the canal rays in a direction at right angles to their motion. A moistened cotton pack around the window seals served to prevent the sealing wax from softening during operation of the tube.

To prevent sputtering beyond the cathode in the region of the windows, a perforated glass disk slightly smaller than the inside diameter of the main tube was slipped into position about five millimeters from the cathode and held there by projections from a phosphor bronze strip encasing the disk. The canal rays passed through the coaxial holes in the cathode and disk and impinged upon the end window. With this arrangement there was very little sputtering beyond the cathode.

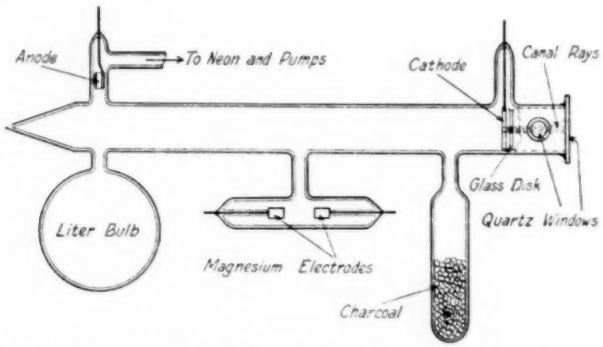

Fig. 1. Discharge tube used for observation of canal rays in neon.

The main tube was connected near the anode to the pumps and to the neon supply. The pumps were operated while the glass walls, electrodes, and charcoal trap were being outgassed. To aid in purification, magnesium electrodes in a side tube were heated until some of the metal evaporated. With the deposition of a magnesium coating upon the walls around the electrodes, the whole tube system became very "hard." The charcoal trap which had previously been heated dull red was next cooled and immersed in liquid air. Neon was then admitted into the tube. After several flushings with the discharge passing between the aluminum electrodes the neon was found to be very pure and could be maintained so for five or six hours provided liquid air was kept constantly around the charcoal trap.

At the low pressure most desirable for operation, the neon "cleaned up" rather rapidly requiring renewal from the supply. A liter bulb sealed to the main tube served to increase the amount present at any one time. With the tube connected always to the pumps and neon supply it was possible to add neon as desired. Small amounts, after having the mercury vapor condensed in the trap shown in Fig. 2, were let into the discharge tube.

The pressure most favorable for producing a sharply defined canal ray-stream was found to be just slightly higher than that pressure at which the discharge failed to pass with a potential of twenty-four thousand volts. To maintain this pressure neon was added at about hourly intervals.

The electrical circuits external to the discharge tube and the positions occupied by the spectrograph with respect to the tube are shown in Fig. 2. The high voltage necessary for operation at low pressures was supplied by a transformer in conjunction with a kenotron tube for rectification. The cathode was grounded. A calibrated spark gap was placed in shunt across the electrodes, and during exposures this was set so that the highest tube voltage would be twenty-four thousand. Except by observation of the discharge during exposure, no provision was made to prevent the potential difference across the tube from falling below any definite minimum value. Previous observations at various low pressures showed how the appearance of the discharge and particularly of the canal ray stream varied with the potential difference across

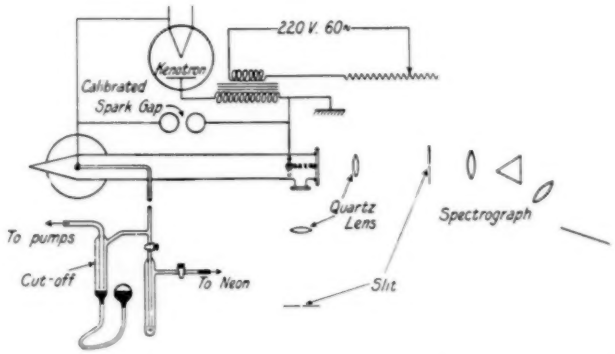

Fig. 2. Diagram showing electrical circuits, method of admitting mercury-free neon, and the spectrograph.

the electrodes, and during operation only such a small amount of gas was allowed in the tube as to produce an appearance corresponding to a voltage nearly twenty-four thousand. At this voltage the velocity of neon atoms calculated from the relation $Ve = \frac{1}{2}mv^2$ is about 5×10^7 cm per second.

Photographs were made with the type E 3 Hilger spectrograph. This instrument is fitted with a quartz lens and prism system throughout, and gives a dispersion of about ten Angstroms per mm at 2600A, and thirty-five angstroms per mm at 4000A. The spectrograph slit width was between two and three hundredths mm, being slightly wider for the side exposures where the intensity upon the slit was less.

For end on exposures a quartz lens focussed the image of the hole in the cathode upon the slit. Exposure times of three hours in this position produced on the plates all except the faintest neon lines throughout the portion of the spectrum under investigation. Side exposures required double this time. Eastman 40 plates were used for all exposures.

RESULTS

Both the end on and side photographs were made on the same plate with the spectrograms close together for comparison. The spectrograph was

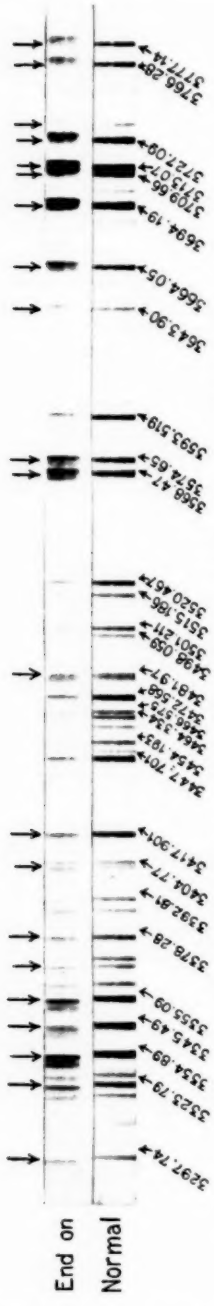

Fig. 3. An enlargement from the original spectrograms showing numerous Doppler effects in neon between 3280A and 3780A. The arrows point to the Doppler effects.

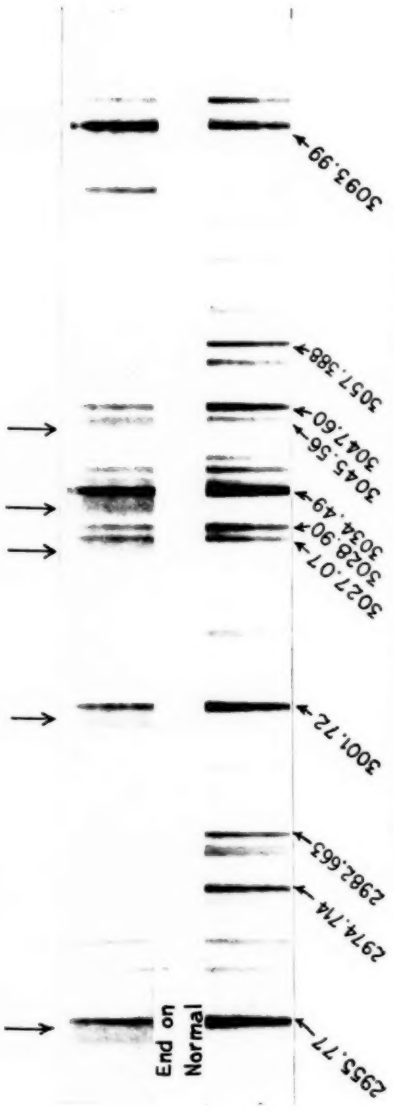

Fig. 4. An enlargement from the original spectrograms showing several Doppler effects in neon between 2950A and 3100A.

equipped with a scale which gave approximate wave-lengths and facilitated identification of the lines.

Fig. 3 shows an enlarged portion of the original spectrograms with numerous Doppler effects indicated by arrows. The broadening in the end on spectrogram is toward the violet since the canal rays were moving toward the slit. In the end on spectrogram of Fig. 3. there are a number of rather sharply defined arc lines indicated (3447.701, 3454.193, 3464.334, 3466.575, 3472.568, 3498.059, 3501.211, 3515.186, 3520.467), for which the effect is clearly absent. Other Doppler lines exist in the end on spectrogram with less intensity than some of these arc lines. It is apparent also that overriding of the Doppler intensity upon other lines occurs where several lines are very close together. In such cases one can generally tell by microscopic examination which of the lines display Doppler effects.

A second enlargement of the original spectrograms between 2950A and 3100A is shown in Fig. 4. The diffuse broadening toward the violet which is quite noticeable in several lines extend over about three and one half Ang-

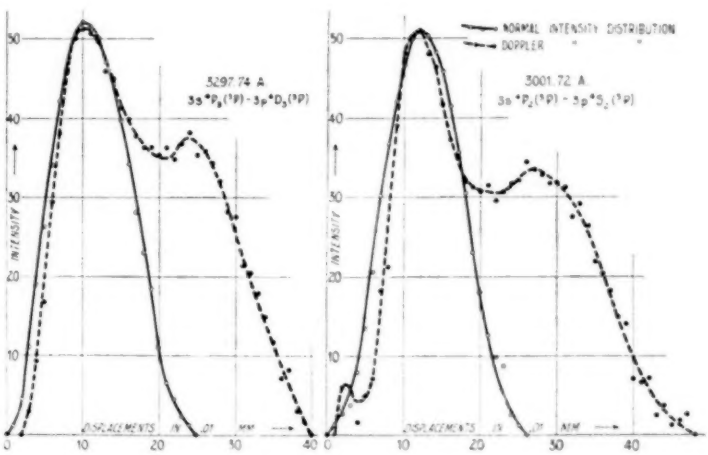

Fig. 5. Curves showing intensity distribution in two Doppler lines as measured by a photoelectric photometer.

stroms. The observed maximum shift is thus only about two thirds the shift one would expect for particles traveling with a velocity of 5×10^7 cm per second, as calculated from the Doppler relation. This discrepancy is commonly observed with ordinary canal rays as the particles fall through only part of the potential applied to the tube.

Photometric measurement of the intensity distribution in several lines was made and the results illustrated in Fig. 5. The photoelectric photometer used was built by Dr. Elmer Dershem, who intends to publish a description of the instrument. A narrow slit about 0.02 mm was moved transversely across a line in steps of 0.01 mm. Intensities were measured by time intervals required for an electrometer gold leaf to move across a fixed portion of eye piece scale. The dashed lines which represent the Doppler lines in Fig. 5 indicate the general trend of Doppler intensity distribution and display the minima which usually exist between the Doppler effects and their undisplaced lines.

The wave-lengths of the lines were identified from Paschen's tables and the tables for the spark spectra of neon given by L. Bloch, E. Bloch, and G. Déjardin. It was at once apparent that, almost without exception, the lines in the first table were accompanied by no Doppler effect lines, while the lines of the spark spectra all showed Doppler effects. The complete list of Doppler effects in neon between 2500A and 4000A is given in Table I. The lines showing the strongest Doppler effects are put in the first column and the lines with

TABLE I. *Doppler lines.*

Strong definite Doppler effects			Faint Doppler effects			Doubtful on account of faintness (F) or overriding (R)		
2792.04	(4)	II	2590.01	(7)	III	2593.57	(6)	III F
2955.77	(7)	II	2610.04	(5)	III	2595.66	(6)	III R
3001.72	(7)	II	2613.41	(4)	III	2615.86	(4)	III F
3027.07	(4)	II	2677.90	(5)	III	2678.65	(3)	III R
3034.49	(5)	II	2756.68	(3)	II	2785.28	(3)	III F
3198.58	(6)	II	2762.97	(3)	II	2794.22	(3)	II R
3218.22	(8)	II	2809.51	(4)	II	3028.90	(4)	II R
3229.58	(3)	II	2835.233	(3)	I	3047.60	(6)	II R
3230.13	(5)		2866.60	(6)	III	3093.99	(4)	II R
3244.15	(5)	II	2910.11	(2)	II	3232.38	(3)	II R
3297.74	(8)	II	2910.44	(2)		3311.32	(4)	II R
3323.79	(7)	II	3045.56	(3)	II	3357.89	(12)	II R
3334.89	(10)	II	3054.70	(5)	II	3360.63	(5)	II R
3344.44	(5)	II	3070.99	(2)	II	3406.88	(5)	II R
3345.49	(3)		3118.00	(4)	II			
3355.09	(7)	II	3164.42	(3)	II			
3367.25	(6)	II	3213.77	(3)	II			
3378.28	(5)	II	3214.33	(5)				
3417.901	(10)	I	3224.84	(5)	II			
3418.002	(6)		3309.78	(3)	II			
3481.97	(6)	II	3319.76	(3)	II			
3568.47	(6)	II	3327.22	(5)	II			
3574.65	(5)	II	3388.47	(5)	II			
3643.90	(5)	II	3392.81	(7)	II			
3644.87	(3)		3404.77	(4)	II			
3664.05	(9)	II	3542.89	(7)	II			
3694.19	(10)	II	3734.94	(17)	II			
3709.66	(7)	II	3751.25	(4)	II			
3713.07	(10)	II						
3727.09	(9)	II						
3766.28	(8)	II						
3777.14	(8)	II						

faint Doppler effects in the second. The third column contains lines where existence of a displaced line is probable but not absolutely certain because of the faintness of the lines or from overlapping of the lines. The number in brackets after each wave-length indicates the intensity of the line and the Roman numerals II, III indicate the first and second spark spectra. Only two strong arc lines were found to show any Doppler effect. These appeared on all plates. In argon it has been shown by Friedersdorff that with potentials greater than 36,000 volts only the lines of the blue spectrum show Doppler effects, while at lower voltages, Doppler effects also appear with the lines of the red spectrum. It is possible that at low voltages Doppler effects might be observed with the arc lines of neon. The analysis of the neon spectrum into

arc and spark lines shows that at the voltages used in these experiments the canal ray bundle in equilibrium consists almost exclusively of singly or doubly charged particles and does not consist of a mixture of positive and neutral particles as in most gases.

No certain indications of several maxima were observed as found in argon by Stark and Kirschbaum[7] and by Friedersdorff. In neon Aston[8] observes singly and doubly charged neon atoms but does not give the relative intensity of the doubly charged atoms. It is probable that there is an equilibrium established between the doubly and singly charged atoms, so that in each displaced spark line there is superimposed a faint intensity from some atoms moving with a higher speed due to their original acceleration as doubly charged atoms.

The author respectfully acknowledges his indebtedness to Dr. A. J. Dempster, under whose direction the work was carried on.

[7] Stark and Kirschbaum, Ann. d. Physik **42**, 266 (1913).
[8] F. W. Aston, Isotopes, 66.

THE VELOCITY SPECTRUM OF NORMAL GASEOUS IONS IN AIR AND THE PROBLEM OF IONIC STRUCTURE

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(Received September 12, 1930)

Abstract

A consideration of the evidence as to the existence of the so called spectra of ion mobilities recently reported by various observers combined with experimental results of the writers indicate that while ions at ages of from 0.5 to 2.0 seconds show marked ranges of mobilities this is not necessarily the case for the normal ions studied over shorter time intervals. It is shown from the recent work of Loeb and the more recent results of Luhr that ions probably consist of one or two molecular addition products of an active type of molecule which pick up the original charged carrier as a result of electrochemical forces depending on the molecular constitution and the sign of the charge. Such products may be present in traces as impurities or may be produced in air by the ionizing agent. The rate of formation of the velocity spectrum therefore will depend on the relative stability of the various ion addition products and the relative and absolute concentrations of the active molecules. Hence the appearance of such a spectrum will vary with the age of the ions and the experimental conditions. It is believed that the greater portion of the lowering of the mobility of the ions below the theoretical value deduced by the assumption that the neutral molecules are not attracted by the ions is due to the usually assumed force of dielectric polarization as utilized in the complete Langevin equation. While the law utilized is not accurate for close approach of ion and molecule (i.e. to one or two atomic radii) it suffices at greater distances. The effect of the electrochemical combinations mentioned above are superposed on this general attraction and lead to an explanation of the differences of positive and negative mobilities and to the three fold lowering of the recombination coefficient on long aging without a very significant (10 percent) change in the ionic mobility recently observed by Luhr and Bradbury.

Introduction

IN A recent article one of the writers (Loeb)[1]* pointed out the necessity for a decision on the question of the reality of the existence of what might be termed a spectrum of mobility among the normal positive and negative gaseous ions. In recent years there have been many papers which on various grounds indicated the possibility that the gaseous ions usually measured had instead of a unique mobility a sort of distribution curve of mobilities confined between narrow limits and centered about some more probable value.[2,10] The *critical* study of the problem has however been confined to but a few observers.[11,12] The diverse results obtained and conclusions drawn, (extending from the notion of a large number of separately resolved mobilities[3,5] through the notion of a continuous band or spectrum of mobilities[6,7,8,10,11,12,18] down to that of a unique mobility,[1] have indicated the existence of a lack of

* Numbered references appear in bibliography on page 1728.

critical control in some cases. They have further indicated a rather wide range of experimental conditions sometimes offering obstacles to any careful critical investigation and at other times causing such a real difference in physical conditions as to make a comparison of conclusions impossible.

In view of the fact that the experimental work of the writers' appeared at least in part to be in conflict with the very careful work of Zeleny[11] and of Fontell[12] a critique of the writers' work was undertaken with results which will constitute a portion of this paper. The conclusions reached from this analysis together with other recent results including those of Luhr[14] make possible a general interpretation of the nature of gaseous ions which serves to clarify a number of hitherto obscure points. It is the purpose of this paper to present these results and conclusions.

The Existence of a Mobility Spectrum

A. Previous investigations

The first notion as to the existence of mobility spectra among the ions doubtless arose in the study of the slow or Langevin ions whose heterogeneous nature led to the observation of such spectra.[2,3,4] The application of this concept to the case of normal ions in air doubtless began as a result of more recent modifications of the air blast methods to normal ions,[2,3,17,18] although as early as 1915 Haines[13] reported to have observed separate groups of normal ions in H_2. The air blast methods utilized what was assumed to be a narrow slab of ionized air and this when caught on a collector of narrow but finite extent as a result of a transverse electrical field led at once to current-potential, or current-down stream distance curves of such shape and width that the assumption of a spectrum of mobilities was inevitable. No critical study of these curves, however, was made and little significance was placed on such curves until the experiments of La Porte[6] using a sort of Fizeau toothed wheel method. This study which was a pioneer investigation in which a critique of the various sources of error was made gave a continuous spectrum of a wide scope of mobilities in air for both ions. In the method ions generated by alpha particles from an intense polonium source were driven through a region between two plates with constant field and received at the other end by an ion collector. The entrance of the ions into the measuring field and their reception at the collector after the lapse of a given time was regulated by a rotating disk in the apparatus having slits which passed the slits in the entrance and exit ends of the constant field. The variation of ion current to the collector as a function of speed of rotation, or as a function of the constant field, gave curves starting at zero rising to a maximum and falling again to zero. The method in itself was bound to give curves of this sort. The extent of the velocity, and hence mobility, range of ions studied was however such as to indicate that there was a real range of mobilities present. In view of the fact that the range observed by La Porte was markedly greater than that observed by the later observers[11,12] using methods in which the control of disturbing variables is simpler; in view of the impurities present due to large quantities of ebonite and the circulating action of the rotating

shutters on the gas; finally owing to what appears to have been an inadequate correction for diffusion it is doubtful whether too much reliance can be placed on this apparent spread as evidence of a spectrum, although the results appear to point significantly towards the existence of such a spectrum.

Following La Porte's work there have been published two further papers utilizing what is essentially a Fizeau method. In these cases, however, the shutters were electrical instead of mechanical. These are the experiments of R. I. Van de Graaf[19] and of Tyndall, Starr and Powell.[8] Both groups of workers admitted the ions to the constant field and from it to the collecting chamber by means of properly timed alternating potentials, actuated by commutators or transformers. Unfortunately in both these experiments the sharpness of the boundaries of the ionized groups of gases entering the field were limited by the fact that the auxiliary alternating fields used interacted with the fixed driving field through gauzes. Despite certain criticisms leveled at the explanation[21] it is an experimental fact that two fields of opposing sign so interpentrate through the meshes of a gauze, (in ion mobility work large mesh gauzes are generally used because of the high absorption coefficient of finer gauzes for the ions), that the equipotential surfaces may well bulge considerably in one sense or the other through the gauzes. Hence at the zero of time when the ions start moving they do not start at the same level but may have a distribution extending a mm or two ahead of or behind the gauze, depending on whether auxiliary or driving field is the greater. The ions are only able to reach to the equipotential surface during the retarding field and are allowed to accumulate there during that period except for diffusion. Such nonplanar distributions of ions act materially to distort and enlarge the extent of the velocity spectra observed. This difficulty was unquestionably recognized by Tyndall, Starr and Powell, who did not attempt to ascribe too much significance to the width of their ion spectrum.

More recently Fontell[12] in his doctor's dissertation has made a most careful study of the reality of the existence of a mobility spectrum among the ions in air. His work was exceedingly carefully controlled and in principle constitutes a method which is perhaps one of the most sensitive used. In this method a thin beam of x-rays ionizes the air near one plate of a condenser system for a short time interval, the ions being in a field. Thereafter the ionized air is driven by the field to a collecting electrode where the current due to the ions is measured as a function of the time by an amplifying system and galvanometer devised for other purposes by Wassastjerna. Under these conditions the ion group is spread apart by the field in transit so that at first only the fastest ions reach the collector but gradually the slower ones and some faster ones liberated later in the cycle reach the collector. From the record of the galvanometer deflection as a function of time by means of a complicated reduction system, Fontell obtains the actual mobility spectrum of the ions caught. The work carefully corrects for diffusion, self repulsion, width of x-ray beam and similar effects. It covers ages of ions ranging from 0.3 to 4.0 seconds and in this sense coincides well with the ionic age range involved in Zeleny's work.

Another most careful and critical of the recent investigations is that of John Zeleny,[11] using ions in air from the room with water vapor present, an age range of the order of 1 second and an air blast method. In this investigation most sources of error have been critically analyzed with the possible exception of the action of the moving air stream in aspirating more ions (and perhaps a larger spatial extent of ionization) into his chamber than is evident from the measurements. When the spectrum obtained using mobilities is compared to that due to the geometrical considerations and corrections are made for diffusion there is in these ions an unexplained spectral width indicating ions existing in air with mobilities spread from 1.03 to 1.48 for the positive and 1.68 to 2.18 for the negative ions. In view of the fact that the corrections are as great as the observed differences perhaps too much emphasis cannot be placed on the *exact* values of the spread of the spectrum. That there definitely appears to be a spectrum is, however, most significant and it coincides in general extent and for the same ion age with that inferred by Fontell from his data.

B. Investigations of the writers

One of the writers (Loeb) has in the past been one of those who have remained somewhat skeptical of the reality of a mobility spectrum. The recent results of this writer[22] on the change of the mobilities of Na^+ ions with time and certain results in this laboratory to be mentioned have led to a more critical analysis of all the evidence at hand, with the result that this article has been written. The reason for the skepticism lay in the observations of Loeb[23] on mobilities of photoelectrically generated negative ions using the original Rutherford A.C. method under carefully controlled conditions. In this method if ions of a unique mobility k exist the ratio of the A.C. ion current i to the half saturation current i_0 can be deduced by theory to be given by $i/i_0=(V-V_0)/V$, where V is the potential applied to the condenser and $V_0=D/kT$, where T is the half period of the square wave and D is the plate distance. The actual i/i_0 curves obtained experimentally on ordinary dried air in 0.1 second or less, under these conditions agreed so closely with theory that the possibility of the existence of more than a single mobility seemed rather remote. The recent work of Fontell and Zeleny led, however, to an investigation of the resolving power of this method with the following results.

One can assume that ions are generated with mobilities ranging from k_1 to k_2 distributed equally over this range of mobilities. An alternating potential of amplitude V is placed across the plane parallel plates separated by D cm. Ultraviolet light is liberating ions continuously from the one plate at a rate of i_0 ions of all sorts per second. The field driving the ions across D is on for a time T, after which ions liberated too late in the phase, or of mobility too low to reach D are swept out of the space by a strong reverse field. It is now necessary to see how many ions the upper collecting plate will collect as a function of V, T and D. The current i relative to the saturation current i_0 in this case compared with that given for a single class of ions will then give an idea of the resolving power of the method. To make such a comparison one may reason as follows.

If ions are uniformly distributed in a band between k_1 and k_2 (an assumption probably contrary to fact but producing negligible errors as far as this question is concerned) the $i_0 dt$ ions emitted in dt seconds will in a time t be distributed over an area $V(k_1-k_2)\ t\ dt$ in the x, t diagram of Fig. 1. Here V is the field strength across the plate S. The fast ions k_1 will be at $x_1 = Vk_1t$ and the slowest ions at $x_2 = Vk_2t$. The density ρ of ions in this strip dt wide will then be $\rho = i_0 dt/V(k_1-k_2)t\ dt$. In the ensuing intervals dt beginning at $t=t$ and going back to $t=0$ the successive areas containing the ions in the $x-t$ plane will present the appearance of the shaded triangle AOB indicated in the Fig. 1. From $x_1 = Vk_1t$ to $x_2 = Vk_2t$ the ions will be contained in a triangular

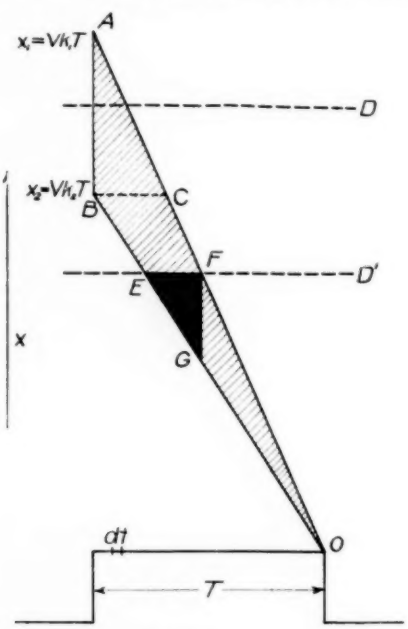

Fig. 1.

element. ABC. Within this element the number of ions reaching a certain distance D will be given by the area of the triangle intercepted between $x_1 = Vk_1T$ and $D = x = k_1Vt$. Hence the *initial* increase of charge received by a plate at a point D will be parabolic beginning at a mobility k_1. At a time such that $D = Vk_2T$ all the ions in ABC will have reached D. From then on the number of ions is distributed in the space time diagram inside the triangle bounded by OBC. At any value of x below $x_2 = Vk_2T$ the number of ions is constant and equal to i_0. The curve for the quantity reaching D as a function of t between $D = Vk_1T$ and $D = Vk_2T$ is then given by the integral

$$Q = \int_{D/Vk_1}^{T} \frac{i_0(Vk_1t - D)dt}{V(k_1 - k_2)t}$$

which includes the density of ions as a function of t.

$$Q = \frac{i_0}{V(k_1 - k_2)}\left[(Vk_1T - D) - D\log\frac{k_1VT}{D}\right].$$

As $Q/T=i$ and calling $k=D/VT$ between limits $k_1>k>k_2$ we have

$$i/i_0=\frac{1}{k_1-k_2}\left[k_1-k\left\{1+\log\frac{k_1}{k_2}\right\}\right] \tag{1}$$

This gives i/i_0 as a function of the variable k between the limits k_1 and k_2. Here k can be espressed as a f (D, V or T) and for each k the i/i_0 can be expressed as a f (V) by calculating the value of k corresponding to each V for D and T constant. Beyond time intervals for which ions of mobility k_1 and k_2 reach D we can express the quantity Q in terms of the area $ABEF$ represented by the smaller distance D' in the figure. This area is the area of the whole triangle ABO less the area of triangle OEF, or better the area of triangle ABO less the area of triangles OFG and GEF. Hence we can write that for a plate D' the quantity is given by

$$\text{Area } ABO = i_0T$$

$$\text{Area } OFG = i_0(D'/k_1V)$$

$$\text{Area } EIG = \int_{D'/Vk_1}^{D'/k_2V}\frac{i_0(D'-Vk_2t)dt}{V(k_1-k_2)t}=\frac{i_0}{V(k_1-k_2)}\left(D\log\frac{k_1}{k_2}-D-D\frac{k_2}{k_1}\right).$$

Whence the quantity Q received by D' under these conditions is

$$\begin{aligned} Q &= i_0T-\frac{i_0D}{k_1V}-\frac{i_0}{V(k_1-k_2)}\left(D\log\frac{k_1}{k_2}-D-D\frac{k_2}{k_1}\right)\\ &= i_0T-\frac{i_0D}{V(k_1-k_2)}\log\frac{k_1}{k_2},\ \text{whence } i=Q/T,\\ i &= i_0\left(1-\frac{D}{VT(k_1-k_2)}\log\frac{k_1}{k_2}\right). \end{aligned} \tag{2}$$

Putting $k=D/VT$ between the limits $k_2>k>0$ we get for the current ratio after the slower ions begin to cross the relation

$$i/i_0=1-\frac{k}{k_1-k_2}\log\frac{k_1}{k_2}.$$

At $k=k_2$ the Eqs. (1) and (2) are the same. As k_1 approaches k_2 the Eq. (2) becomes $i/i_0=1-D/kTV$ which is the simple equation $i/i_0=(V-V_0)/V$ given above for a unique mobility.

An idea of the resolving power of this Rutherford A.C. method as applied to the case of ions with mobilities lying between $k_1=2.2$ and $k_2=1.6$, as observed by Fontell for negative ions is shown in Fig. 2. There i/i_0 as computed from the above is compared with the curve i/i_0 computed for ions of a single $k=1.9$, the average value. It is seen that the difference is not very marked and the resolving power is small. In Fig. 3 is a typical result, previously published[23] obtained by Loeb for nearly identical conditions for dry air $T=0.0275$ at atmospheric pressure. D was 1.41 cm. in this case and

negative ions from a plane photoelectric source were used. The observed curve in this case shows no asymptotic foot within the limits of accuracy of the method.

As Zeleny[11] correctly points out, these results should have been corrected for diffusion. However, the correction becomes small in time intervals of 0.02

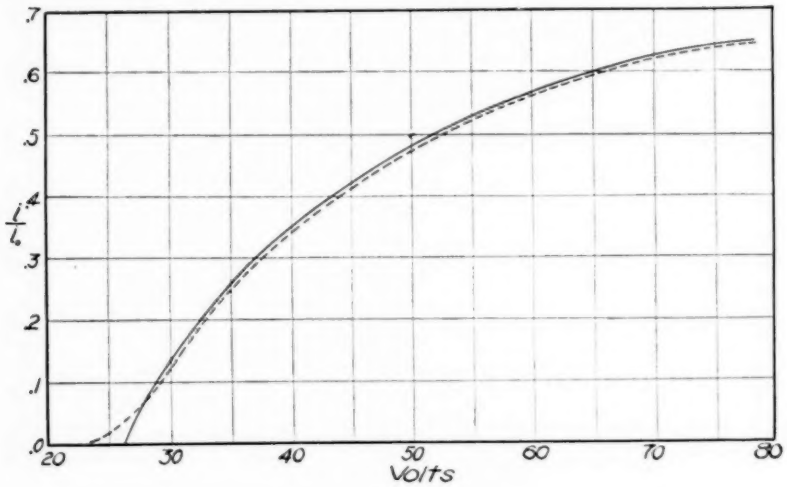

Fig. 2.

seconds and in any case the presence of notable diffusion would have yielded asymptotic feet. This may in part account for such feet at longer times of passage as observed.

It appears from the above that the method as used is a highly insensitive one for indicating the existence of mobilities spread over a more limited range

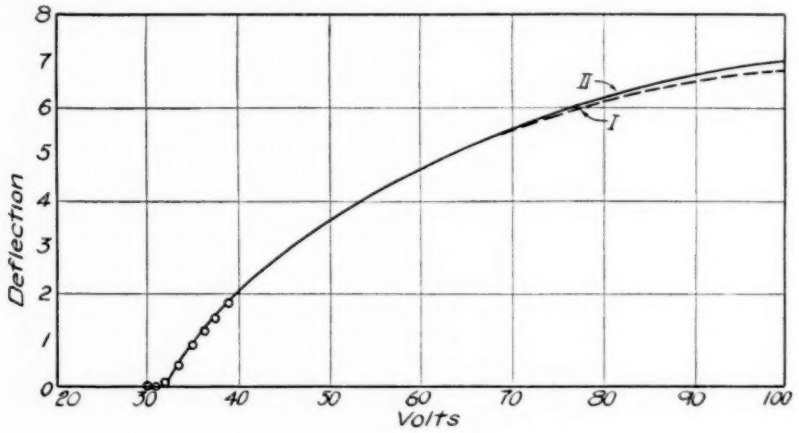

Fig. 3.

of values. Perhaps the best conclusion that can be drawn on the basis of this work is that with *dry air, photoelectric ions* (no great amount of chemical products e.g., ozone and nitric oxides are formed by the ionizing agent) and in *shorter time intervals* the spread of the mobility spectrum is even without

corrections for diffusion distinctly less than that observed by Zeleny and Fontell at *longer* intervals of time and under different conditions.

There is a chance that by using a differential method, i.e., measuring the *current at each instant* during the cycle instead of the *integrated current*, as was done by Fontell, a much more significant result might be obtained. This is, however, at present experimentally impossible. A better result than the one above could be obtained by using an ionizing flash of ultraviolet light which is short in duration compared to T. Such a curve could be analyzed to get the form of the distribution if with very sensitive measurements the derivative of the curves obtained in this fashion were determined graphically. Such an experiment is to be undertaken in the near future.

An almost exact analogue of this proposed method has been carried out by J. L. Hamshere[10] in an admirable investigation. Hamshere used ions generated by polonium and driven into the measuring field by means of an auxiliary gauze and plate in the generating chamber. The apparatus was so arranged that the auxiliary field as used in the Franck modification of the Rutherford A.C. method was put on so that just at the beginning of the phase driving the ions from the origin towards the collecting plate this auxiliary field was put on for but a short time. This gave a burst of ions through the gauze into the measuring field which then was spread into a velocity spectrum by the field. The current reaching the upper plate then depends on the distance D, the duration T of the positive or driving field acting on the ions before the field reversed, and the field V applied. The process is then repeated. This method except for the use of polonium as an ionizing agent and the gauze, instead of a photoelectric source is the one suggested above. However, in spite of Hamshere's use of the high auxiliary field, as had been suggested by the writer,[23] to avoid the effects of the initial displacement of the ions due to interpenetration, (his gauzes had wide meshes of 1 mm) it is most probable that much scattering of the origin of the ions at the beginning of T must have resulted from this procedure. Further the intense polonium ionization as we shall see produces ideal conditions for formation of products which are active on the ions. Again no attempt at correction for diffusion was made. Finally one of the writers in all his work with methods of this type never observed the type of intercepts obtained by Hamshere on the high mobility side of his curves which are neither intercepts of the abrupt type to be expected from unique mobilities, nor intercepts of a truly asymptotic character which would be expected. It appears as if some spurious effect must have subvened to cause these curves. Perhaps this was due to accumulations of ions at the equipotential barriers in the meshes while the reverse field was on. The curves obtained by Hamshere were then graphically differentiated to give the mobility spectrum. In general they agree with the type of curves of Zeleny and Fontell. They appertain, however, to ions of much shorter life than the ions of the latter observers. In view of the conditions mentioned and in view of Bradbury's results to be discussed it appears to the writers that while Hamshere has devised an ideal method in principle, the work should be carried out with the photoelectric

method before too much credence can be placed in an interpretation of these curves as representing a true velocity spectrum of ions over short time intervals.

While the results of Loeb on the absence of a broad mobility spectrum over short time intervals are not entirely convincing, even admitting the possible sources of difficulty in Hamshere's work, the conclusions arrived at are substantially borne out by recent work of Bradburg[16] using the method of Tyndall and Grindley.[24]

The mobility of gaseous ions in dry air of considerable purity and also of normal purity has recently been investigated by one of the authors (Bradbury). In these experiments the alternating current method devised by Tyndall and Grindley[24] with intense x-ray ionization was employed. This is a

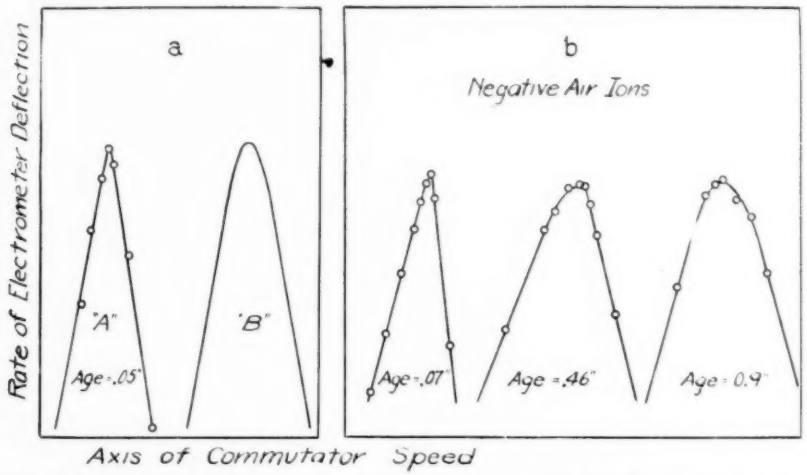

Fig. 4. (a) Curve A is a typical curve for positive ions of age equal to 0.05" giving a value for the mobility of 1.60. Curve B is the theoretical curve to be expected if the mobilities were distributed over a ten percent range on either side of the accepted value. (b) A series of typical curves for negative air ions of increasing age, showing the change to a type of curve corresponding to B in Fig. 1 and giving evidence of a spread of mobilities.

"peak" method, and the mobility is calculated from the position of the maximum in the ion current curve as the time of alternation of the field is varied. The mathematical theory of this method has been developed by Tyndall and Grindley. It appears from the integrals relating the ion current to the time of one complete cycle that the sides of the peak should be straight lines, intersecting at a point, by the position of which a mobility is uniquely determined. In practice this is not always the case. Even when new ions are studied, the sharp peak will be slightly rounded off by diffusion, self-repulsion, and other factors arising from the measuring instruments themselves. In addition to this if the time, the time $(\delta-\gamma)T$, of retardation of the ions being measured towards the lower plate is too great, or the position of ionized band between the plates is too near the upper plate, at the higher and lower frequencies of alternation, ions of the opposite sign will begin to reach the upper plate. This causes the measured current to decrease more rapidly than

that predicted by the simple Tyndall and Grindley equations and an outward curvature of the sides of the peak results. Since the curving was never found to influence the position of the maximum, no great care was taken to avoid this condition in the effort to obtain ion currents of measurable intensity. However, by varying the conditions of δT, V_r, and the slit width (width of ionized beam) the sides of the curve could be made quite satisfactorily straight as seen in Fig. 4. It seems in view of such curves of interest to consider the resultant shape of the Tyndall-Grindley curve should there be a distribution of mobilities between certain limits. In other words, it is important to see what the effect of a continuous distribution of mobilities will be on these curves. This can be accomplished by testing the effect of a range of mobilities on the curve shape; a result which can most easily be accomplished, in view of the integrals involved, by a graphical method which sums the ordinates of a series of individual curves over the range of mobilities involved. When this is done we obtain a curve of the shape shown in Fig. 4 a curve *B*. Curve *A* is an experimental curve recently obtained in pure air with x-ray ionization for positive ions of age equal to 0.05 seconds. By combining a series of curves of this shape distributed uniformly over a range ten percent greater and ten percent less than the accepted value (a smaller range than was found by Zeleny) curve *B* was obtained. With sides of the same slope, the rounded top is very apparent. Fig. 4b shows a series of experimental curves for negative ions in less pure gas taken on ions of increasing age, as shown. Comparing these curves with that of Fig. 4a it seems very apparent that ions of age less than 0.08 do not have a spread of mobilities as great as that chosen.

The curves shown indicate quite strikingly two facts. First the ions of shorter life in pure air *do not appear to show any certain indications of a velocity spectrum of any great extent*, (certainly the range is smaller than 10 percent. Secondly at ages greater than 0.1 second the appearance of a range of velocities is quite definite and becomes more pronounced as time goes on. Again as in all methods the resolving power is too small to indicate the nature of the changes occurring but it is clear that such a real spectrum exists. These results strikingly confirm the conclusions to be drawn from the photoelectric method for newer ions and the results of Fontell and Zeleny on older ions. They disagree definitely with those of Hamshere and the results at shorter time intervals of LaPorte.*

Theoretical Conclusions

That this confirmation should occur is not surprising in view of certain theoretical considerations concerning ions together with recent results obtained by Luhr[14] in this laboratory. Luhr has been studying the ions produced in air, O_2, N_2, and SO_2 and other gases by a Geissler discharge after sorting the somewhat aged ions by means of the method of molecular beams and a positive ray analyzer of the Dempster type. While he has as yet not achieved a

* In a recent paper Zeleny (Phys. Rev. **38**, 969 (1931)) has confirmed the absence of a mobility spectrum in air over the shorter time intervals using an air blast method.

study of the really older ions the facts found in air with *high concentrations of the ionization products of discharge* indicate that as the pressure of the gas increases, especially in air, the ions are predominantly of a higher molecular weight than those at low pressures which consist of O^+, O_2^+ and N_2^+ and O^{3+}, etc. These older ions have molecular weights ranging up to 200. They are not in a continuous group of all masses, but *largely consist of single charged molecules of the reaction products of the discharge*, i.e., oxides of nitrogen, nitric acid and where SO_2 is present even H_2SO_4.

It is clear that in any ionized complex gas such as air all sorts of chemical products must be formed in quantities depending on the nature of the ionizing process. Depending on their electrochemical affinity as shown from studies of mixtures[34] certain of these molecules are strongly attracted to ions of one sign or the other. These compounds or attached molecular ions are formed not by the inverse fifth power law attractions but forces between the charged portions of single molecules due to structural characteristics as worked out by researches analogous to those of H. A. Stuart,[25] C. P. Smyth,[26] C. T. Zahn[27] and others. For example the O atom in ethyl ether is highly negative and should strongly attract and attach positive ions, or the positive atom or molecule can combine with an NH_3 molecule to give an ammonium like ion, while the strongly positive H in the OH group attracts negative ions. Now there must be formed a number of such ion complexes *with not more than one or two molecules attached*, in any gas ionized by x-rays or α-rays, in the measure that active molecules are present, and that probability of reaction and number of impacts of ions with these lead to formation of such complexes. The lower the concentrations of these substances the longer times of sojourn in the gas must transpire for such attachments. In gases as ordinarily studied there will even be competition among various molecules for the ions of a given sign. At first a less strongly attracted but more frequent impurity will win, but with age the more strongly attracted but rarer substances will get a large share of the remaining charged atoms. This action is beautifully illustrated in the aging effects observed by one of the writers' for Na^+ ions in N_2 and H_2. and by the aging effects observed by Erikson[17,31] and the action of water vapor, alcohol and ozone on ions in air as observed by Tyndall[24,28] and his collaborators, Mahoney,[30] Valasek,[29], Hamshere[10] and others.

Thus it is to be expected that while the earlier ions are more uniform in structure, and thus of uniform mobility, aging particularly in gases with many chemical products will lead to the predominance of a greater diversity of the ion structures present, with a consequent spread of mobilities. Hence it is not surprising that in gases like those used by Fontell, Zeleny and one of us over long time intervals with the selective action of recombination in some cases removing the lighter complexes, to find quite a velocity spectrum among the ions. With greater resolving powers of our measuring equipment of course the separation of the ion groups should appear, if the spectrum has not too many components, as in Luhr's apparatus. It is also clear that the distribution of mobilities in such a group must be rather more like that found by Zeleny and others than the uniform velocity band utilized in calculations in this paper.

THE DIFFERENCE BETWEEN POSITIVE AND NEGATIVE MOBILITIES

This assumption of the nature of ions at once clarifies many heretofore disturbing phenomena which have been very hard to understand. To utilize this concept let us first restate the situation. It must, and will be maintained throughout, that the *ions are essentially simple in structure* one charged molecule O_2, N_2, O_3, etc., attached to possibly one and perhaps two, but not more, other molecules of appropriate structure. More than one or two attached molecules would so weaken the bonds, with the space limitations imposed by the attached molecules that they would cease to be effective. These attachments must be considered in the nature of loose chemical combinations caused by structural effects, and *not primarily caused by the inverse fifth power law attractions*. In some active organic molecules of high molecular weight, i.e., with large inactive chains of CH_2 groups the effect of this attachment alone will cause marked diminution of the mobility owing to great increase in ion radius. This has been observed by Tyndall[28] and his collaborators with the alcohols and by Loeb and Dyk[32] with the amines.

In the main, however, the very great lowering of the mobilities, to one-fifth the simple kinetic theory value,[35] are due not to this compound formation but to the *apparent increase of the ionic radius due to the attractive forces of the ionic charges on neutral gas molecules*. The main lowering will therefore be ascribable to dielectric attractive forces of the inverse fifth power law type which must hold fairly well at distances of 10^{-7} cm and greater. For closer approach doubtless the dielectric forces are less and this with our understanding of repulsive forces show why the influence of the actual kinetic theory radius as it appears in Langevin's equation may not be as critical as it appears.[1] That these dielectric forces must be the main factor in reducing ionic mobilities to the observed low values is definitely attested by the fact that this Langevin law alone or even the Loeb-Thomson modification and the Wellisch equation as modified by Loeb,[33] give the correct order of magnitude and nearly correct values for the mobilities of the ordinary ions. Hence the mobilities observed are produced by (1) the dielectric attractions which have superposed on them and (2) the increases in mass and actual physical diameter caused by the one or two electrochemically bound molecules.

Granted this postulate we can at once see that the effect of the sign of the charge on mobilities is not in any way to be ascribed to a difference in the dielectric constant for positive and negative ionic force fields.[36] It must be ascribed to the specific electrochemical combinations which result by reaction of positive and negative ions with molecules present in some gases, the negative ion adding the larger molecule in some gases in others the positive ion doing so. If this is true the whole question of the difference of positive and negative mobilities is simplified and may be even extended to the C. T. R. Wilson cloud chamber experiments. The fact that negatively charged droplets condense to visible size much more readily than do the positively charged drops may not need to be ascribed to more intense dielectric forces on the water droplets in the intense radial fields of the small negative drops than on small positive drops. They can now be ascribed to the fact that the

droplet that has picked up a negative ion has also picked up from the negative ion a more hygroscopic addition product than there exist about the positive ions. Thus a droplet such as Thomson postulates, containing 1000 water molecules, that cannot grow at a given supersaturation because of surface tension forces, in picking up a negative $O_2^-(2\ SO_2)$ ion has besides the compensating charge the vapor tension of 20 N H_2SO_3 solution. This may cause more ready condensation on the negative ion than on the positive ion which has no such addition product.

The Recombination Coefficient

Another problem which is clarified by this viewpoint is the apparent difficulty in the different effects of aging on mobilities and recombination coefficients as observed by Luhr[15] and Bradbury.[16] In the intense x-ray ionization reactive substances are formed in the gas in progressively greater amounts on aging. The faster ions owing to lighter mass recombine quickly and leave the slower ions. Now since those reaction products picked up by ions in air are, as Luhr[14] has observed, atoms not of atomic and molecular weights 16 and 32, but some molecules of molecular weights as high as 200, we can see how the value of the recombination coefficient which is inversely proportional to the square root of the mass of the ion can be reduced without materially changing the mobility of the ions. Thus the reduction of the recombination coefficient with time is not due to the formation of a very large cluster ion which is incompatible with a 10–20 percent mobility decrease, but is due to the attachment of a molecule of greater mass without a very much greater radius: Thus the increase in radius of an O_2^+ ion to that of an $(HNO_3)_2O_2^+$ ion is not as drastic an increase in radius as would be that due to an addition of 8 to 12 O_2 molecules in a monomolecular cluster which are loosely bound by dielectric forces.

It is therefore seen that the recent studies of the velocity spectrum of ions together with other recent work leads to a comparatively simple picture of ionic structure and behavior which from its nature and its simplicity cannot be far from true. It is hoped that the clarification due to this analysis will guide future workers to a means of more quickly and completely establishing the obvious conclusions here made.

In conclusion the writers wish to acknowledge their thanks to Dr. H. A. Stuart for the valuable information which he gave concerning molecular structure as it affects this problem, and to Dr. O. Luhr for permission to anticipate the publication of his results.

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THE MASS OF POSITIVE IONS IN A GLOW DISCHARGE

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Abstract

Preliminary results are presented here in an attempt to determine directly the mass of gas ions in air, N_2, O_2, and SO_2. The ions were formed in a glow discharge, allowed to drift at low velocity through a distance of 2.5 cm, and passed as a molecular beam through a slit 0.01 mm by 5.0 mm where the mass spectrum was analyzed with a positive ray analysis apparatus of the Dempster type. The pressure in the discharge and drift spaces was maintained at 0.1 to 0.5 mm of mercury. The following ions appeared in relatively large quantities: N^+, N_2^+, O^+, N_2^+, O_2^+, O_3^+, SO_2^+, and $H_2SO_3^+$. In addition a smear of heavier ions appeared in smaller numbers, though the intensity was greater in air than in the pure gases and, in air, became relatively larger at high pressures. Peaks corresponding to molecular weights of 56–64, 76, 80, 96, 108, 138, 140, 168 and 200 were the most prominent indicating the presence of such ions as $2N_2^+$, $N_2O_2^+$, $2O_2^+$, $N_2O_3^+$ and heavier combinations. N_3^+ and O_3^+ ions apparently play an important role in gas ion phenomena though the N_3^+ is relatively unstable since it breaks up in the magnetic field into $N_2^+ + N$. In view of the results it seems likely that air ions aged over a considerable period of time are of a complex and heterogeneous nature, due probably to the formation of nitric oxides, while the ions in pure gases remain monatomic, diatomic and triatomic except for attachment to impurities.

Introduction

THE most perplexing problem in the field of gas ions to-day concerns the nature of the ions. As a result of extensive and thorough measurements of such quantities as mobility, coefficient of recombination, and attachment coefficient of electrons the behaviour of ions under various conditions is fairly well known. However, it is often difficult to interpret this behaviour correctly as such measurements do not give any direct or definite answer to the question of the mass and composition of the ions. In some cases gas ions may consist of single atoms and molecules, but it seems likely that in most gases as the ions age they become more complex in nature. This supposition is born out by many mobility experiments such as those of Erickson on the aging of the positive ion, those of Loeb on mobility in mixtures, and more recently the work of Loeb[1] on Na positive ions in H_2 and N_2, and that of Bradbury[2] on aging. Such investigators as Zeleny and Fontell in their recent work on the spread of mobilities have shown quite definitely that at any rate after aging about a second, there must be ions of various sizes and kinds present. The possibility that ions of a molecular weight of several hundred occur after aging a second or more was indicated by the recombination experiments of the writer.[3]

[1] L. B. Loeb, Phys. Rev. **38**, 549 (1931).
[2] N. E. Bradbury, Phys. Rev. **37**, 1311 (1931).
[3] O. Luhr, Phys. Rev. **35**, 1394 (1930); **36**, 24 (1930).

Since all angles of approach to the mobility problem have failed to determine definitely the real constitution of the ions it appears imperative that the mass be measured by a direct method. It occurred to Professor L. B. Loeb that the problem might be solved by forming the ions in a glow discharge and employing the Stern method to determine the velocity spectrum in a molecular beam. After consultation with Professor Stern on the feasibility of the method it was decided that accurate measurement with velocities of the order of a fortieth of a volt would be impossible owing to the presence of unknown contact potentials. Professor Stern suggested however, that the problem might be approached by forming a molecular beam as suggested by Professor Loeb and measuring the distribution of masses with a Dempster type of positive ray analysis apparatus. Since the chance of a collision in a molecular beam is very remote the ions should not break up in the analyzing chamber and the masses present could be determined directly. In all previous positive ray analyses the normal ions would be broken up by low pressures and high fields before entering the analyzing chamber. The conditions in a glow discharge cannot of course be strictly compared to those in a gas at high pressures where the ionization is produced by x-rays, polonium or some similar method. However, the intensity of ionization obtained by such means is entirely too small to be measured by a positive ray analysis method when one considers that the ion current must diffuse through a slit of the order of 0.01 by 5.0 mm in size. Normal gas ion conditions can be approximated in the glow discharge if the pressure is kept as high as possible and the ions after formation are allowed to drift through some cm of gas with a velocity so small that any aggregates which might be formed would not be likely to break up on collision with neutral molecules; that is, the result would be the same as though the ions were formed by any other method at high pressures and aged over a very short period of time. It was felt in undertaking the experiment that even if normal gas ion conditions could not be attained useful knowledge would result from the determination of the ionization products formed in a discharge tube operating between 0.1 and 1.0 mm of mercury pressure.

The present results are preliminary in nature and probably give a better idea of the ionization products as formed in the discharge than the nature of normal gas ions. However, particularly at the higher pressures where the effective aging is greater, positive ions of mass larger than a single molecule begin to appear in quantities comparable with the number of charged atoms and molecules. So far no negative ions have been observed even in gases such as oxygen and sulfur dioxide which have considerable electron affinity; but this is not surprising considering the low pressures and hence relatively few collisions which the electrons would make with neutral molecules before being swept out of the volume.

Apparatus and Method

The form of apparatus finally adopted after considerable experiment is shown in Fig. 1. A discharge was maintained between the electrodes *A* by means of a sixty cycle neon sign transformer with a potential of about 4000

volts or as high as could be employed without overheating the tube. About 2.5 cm below the electrodes was a nickel cap G with a tungsten wire grid in the center through which some of the ions formed in the discharge could pass. The grid G and the first slit of the analyzing chamber S_1 were separated a distance of 2.5 cm, the ions drifting through the gas in this space with a field of five volts per cm. The slit S_1 was 0.01 mm wide and 5.0 mm long; so the pressure in the discharge and drift spaces could be maintained at 0.1 to 0.5 mm of mercury while the pressure in the analyzing chamber could be kept down to 10^{-4} mm by continuous pumping.

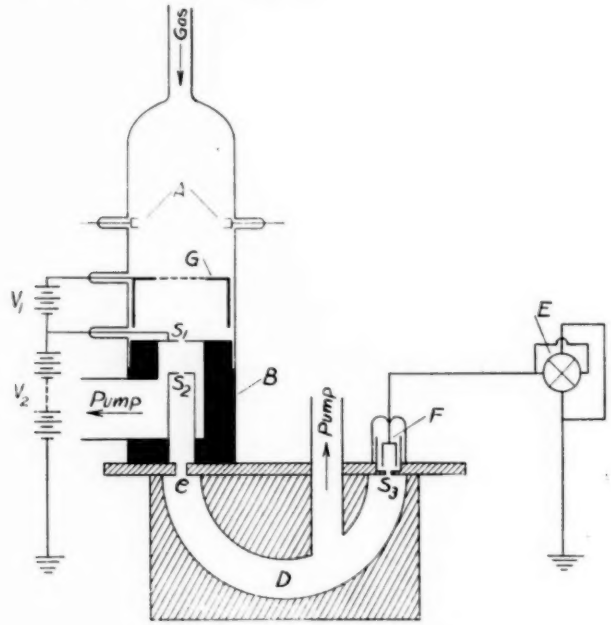

Fig. 1. Diagram of apparatus.

The analyzing chamber, made of brass, was of the standard Dempster type kindly loaned to the writer by Dr. R. E. Holzer and recently described by him.[4] The ions passed through the slit S_1 with a velocity of only a small fraction of a volt, were accelerated by the potential V_2 (100 to 200 volts), bent into a semicircle of 5.0 cm radius by a magnetic field at the point C and collected in the Faraday cylinder F where the charge was measured by the electrometer E. S_1 was insulated from the grounded analyzing chamber by mica and picein wax. B was a soft iron cylinder for magnetic shielding. The slit S_2 was 0.5 mm wide and S_3 about 1.5 mm wide.

The first attempts at measurement were made with an all glass apparatus having the inside walls silvered for electrostatic shielding. The metal cap and grid G were omitted and although some ion current was obtained through the slits S_1 and S_2, the velocities were so heterogeneous due to the high potential discharge that no appreciable current was obtained through the slit S_3. The

[4] R. E. Holzer, Phys. Rev. **36**, 1204 (1930).

glass apparatus was finally abandoned in favor of the metal chamber and a brass plate with a cm hole in the center was used in place of the grid and cap *G*. Still no ions were obtained in the Faraday cylinder as the metal plate did not sufficiently shield the drift space from the high potential discharge. Large ion currents were later obtained by placing a single electrode above the brass plate, the plate itself acting as the other electrode; but in this case the ions were projected through the slit S_1 with a velocity of about 300 volts and the conditions of drift were obviously not fulfilled. Next a filament and grid of the type employed by Smyth,[5] Hogness and Lunn[6] and others was tried and worked very well at pressures up to 0.05 mm, but above that the intensity of ionization dropped to a negligible amount. As it was necessary to work at pressures of at least 0.1 mm and preferably near 1.0 mm this method had to be abandoned. Finally the apparatus shown in Fig. 1 and described above was adopted and gave satisfactory results at pressures of 0.1 to 0.5 mm, though the ion current, especially at higher pressures was relatively small. It is hoped by means of a more intense discharge, faster pumping (hence a wider slit S_1) and more sensitive methods of detection that in the future much higher pressures, longer aging and at the same time larger currents may be attained. Negative ion currents of sufficient intensity to be measured should also be obtained under such favorable conditions.

The gases employed in the experiment were purified by passage through tubes of $CaCl_2$, NaOH, and P_2O_5; and in addition in the case of pure nitrogen through a tube of hot copper to remove the oxygen. The gas then flowed through a capillary, passed through two liquid air traps and into the discharge tube. The liquid air traps precluded the possibility of the presence of any large amount of mercury, water vapor or organic material from stopcock grease, gauges and walls of the tube.

In taking measurements it was found most satisfactory in view of the large range of masses to be covered, to keep the accelerating potential V_2 constant and vary the magnetic field by changing the current through the coils of the electromagnet. The electromagnet was calibrated by means of a flipcoil and Grassot fluxmeter, and the calibration later checked with ions of known mass. A rate of deflection method was employed in measuring the ion currents to the electrometer.

Results

Results were obtained in a number of pure gases and mixtures including N_2, O_2, SO_2, air, SO_2-N_2 mixtures and N_2-ether mixtures. The intensity of ionization in pure SO_2 and N_2-ether mixtures was too small to be measured satisfactorily. Typical results obtained for the other gases are shown in Figs. 2 to 7 inclusive. As the relative intensities of the various ions were extremely sensitive to small changes in the pressure of the discharge it was difficult to check the curves accurately, especially at higher pressures. There was such a smear of ions or larger mass and the intensity was so small that it was difficult

[5] H. D. Smyth, Phys. Rev. **25,** 452 (1925).

[6] T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10,** 398 (1924).

even to check the position of many of the peaks. However, peaks corresponding to certain of the masses appeared so consistently that there can be no doubt of their existence.

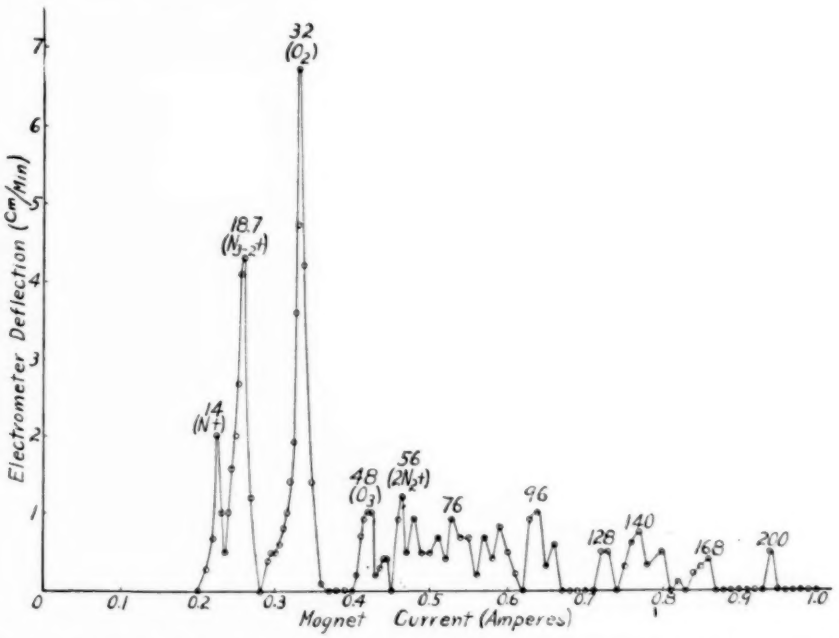

Fig. 2. Results in air with pressure in the discharge tube of 0.075 mm of mercury and accelerating potential V_2 of 150 volts. Numbers above the peaks indicate the molecular weights of the ions.

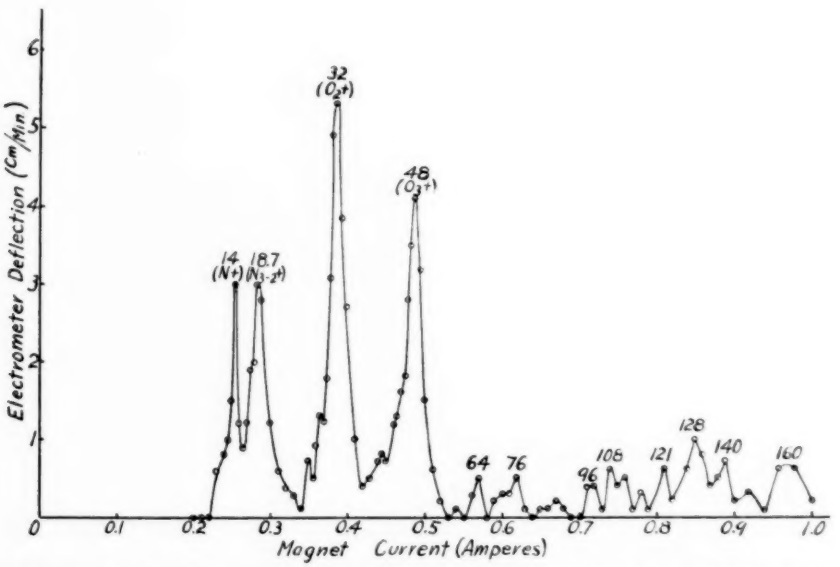

Fig. 3. Results in air with pressure in the discharge tube of 0.10 mm and accelerating potential V_2 of 150 volts. Numbers above the peaks indicate the molecular weights of the ions.

Fig. 2 shows a curve taken in air at 0.075 mm pressure in the discharge tube with an accelerating potential V_2 of 150 volts. The first mass which appears is 14.0 corresponding to N^+. O^+ is absent in measurable quantities, but a strong peak appears at a mass of about 18.7 which can only be accounted for by assuming an N_{3-2}^+ ion which is accelerated in the electric field as N_3^+ and

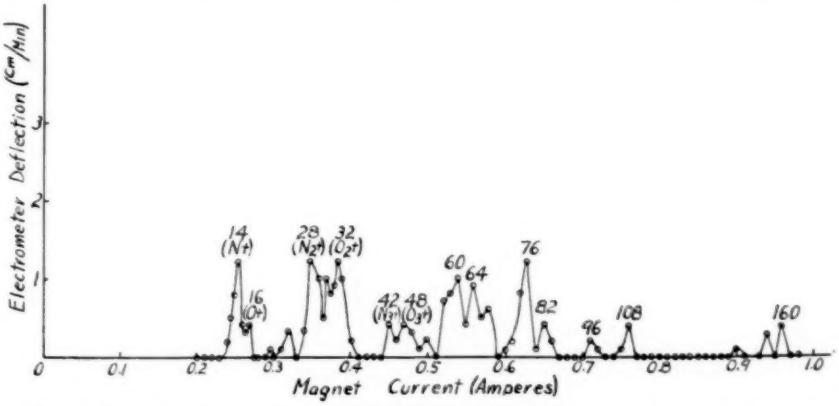

Fig. 4. Results in air with pressure in the discharge tube of 0.400 mm and accelerating potential V_2 of 191 volts. Numbers above the peaks indicate the molecular weights of the ions.

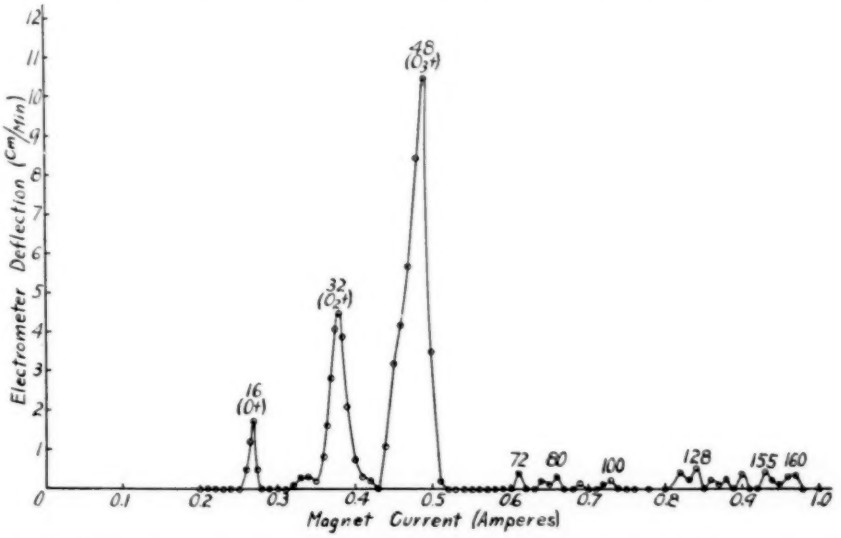

Fig. 5. Results in pure oxygen with pressure in the discharge tube of 0.10 mm and accelerating potential V_2 of 193 volts. Numbers above the peaks indicate the molecular weights of the ions.

breaks up in the magnetic field into N_2^+. This ion may have been observed by Smyth[7] working at low pressures but he attributed the corresponding peak to an impurity, presumably water. In the present work however, the peak occurs at a point corresponding to a mass which is consistently greater than 18. It disappears completely in pure O_2 or other pure gases but is always rela-

[7] H. D. Smyth, Proc. Roy. Soc. **104A,** 121 (1923)

tively strong in pure N_2 or in nitrogen mixtures. In view of the careful drying of the gases and the presence of the liquid air traps there could hardly be suffi-

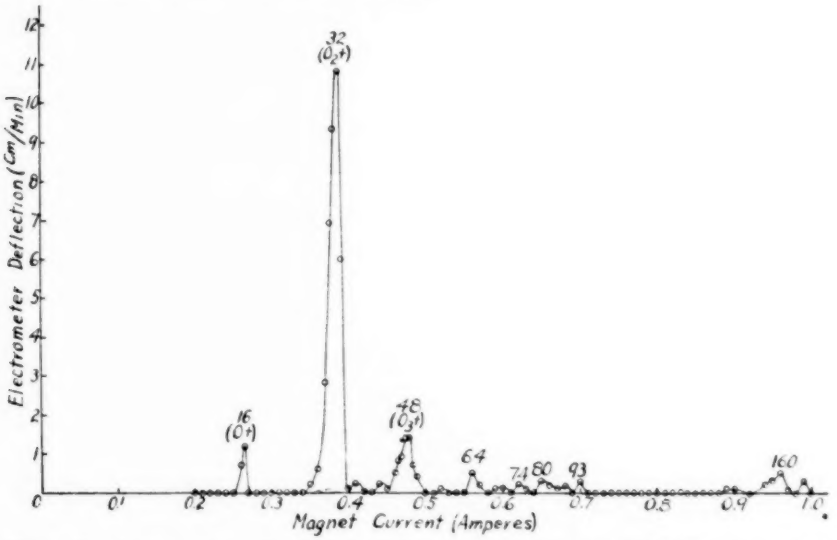

Fig. 6. Results in pure oxygen with pressure in the discharge tube of 0.30 mm and accelerating potential of 193 volts. Numbers above the peaks indicate the molecular weights of the ions.

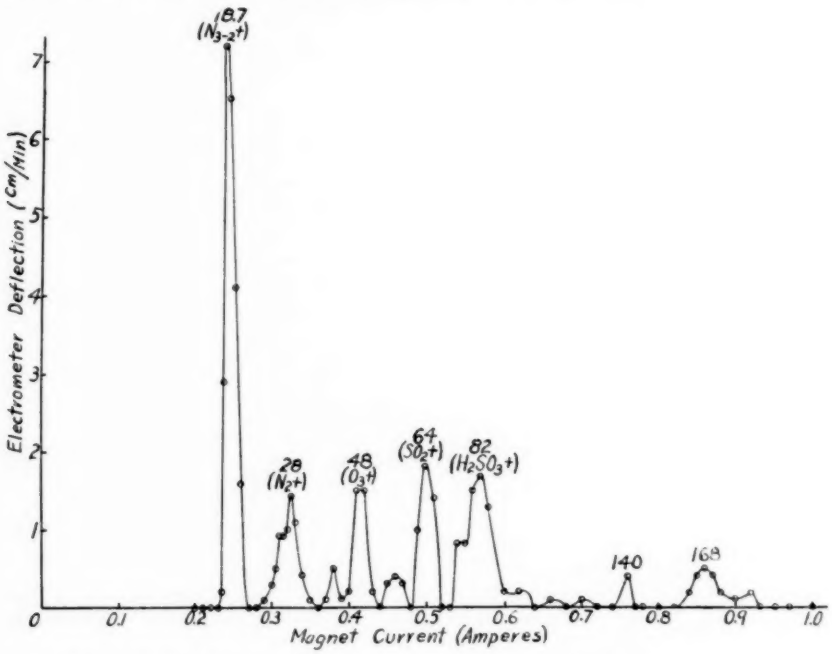

Fig. 7. Results in mixture of fifty percent N_2 and fifty percent SO_2 at a pressure of 0.30 mm and accelerating potential of 150 volts.

cient water vapor remaining to give such intense ionization. The next peak is due to O_2^+, N_2^+ being absent or too weak to measure. O_3^+ appears next as

a definite peak, with masses of approximately 56, 60, 76, 96, 128, 140, 168, and 200 following. These peaks do not stand out very definitely against a smear of ionization in the background, but peaks corresponding to these masses have a tendency to appear again and again in air.

Fig. 3 shows another curve taken in air at slightly higher pressure (0.10 mm). In this case O_3^+ is very pronounced with O_2^+ still the strongest, N^+ and N_{3-2}^+ quite strong and a smear of heavier ions.

Fig. 4 is a typical curve taken in air at higher pressures (0.40 mm). As the pressure increases the intensity of the ions of smaller mass decreases markedly while the intensity of the heavier ions, particularly of masses around 60 and 76 tends to increase. This is of course to be expected as the ions are now aged somewhat longer having made about 400 collisions with neutral molecules before entering the analyzing chamber.

Figs. 5 and 6 show two runs in pure oxygen taken at 0.10 and 0.30 mm pressure respectively. In both cases the number of heavy ions is relatively small, but it is interesting to note that at the lower pressure the O_3^+ peak is much the strongest while at the higher pressure O_2^+ appears to be the principle product of ionization.

Fig. 7 shows the results for a mixture of fifty percent N_2 and fifty percent SO_2. N_{3-2}^+ appears the most intense while N_2^+, O_3^+, SO_2^+ and $H_2SO_3^+$ show up as definite peaks of relatively large intensity. In this case the SO_2 was taken directly from a tank without drying or purifying; so water vapor was undoubtedly present in considerable quantity and may have contributed partially to the N_{3-2}^+ peak.

Measurements in pure N_2 showed N_{3-2}^+ to be the most intense with considerable N^+ and N_2^+ but no appreciable number of heavier ions. As has been indicated previously, no negative ions could be found in any of the gases but this is not surprising since even at the higher pressures of about 0.5 mm the electrons would make only about five hundred collisions in the drift space and only a negligible number could attach to neutral molecules. Small quantities of negative ions formed in the discharge at lower pressures have been observed by J. J. Thomson and Smyth but would probably escape detection in the present experiments due to the relatively low intensity of ionization. No multiply charged ions were found in the work reported here, but it was to be expected that the few doubly charged ions formed in the discharge would lose one of their charges to a neutral molecule while passing through the drift space.

Summary and Conclusions

The results may be summed up as follows: (1) In air, N_2, O_2, and SO_2 the following positive ions give strong definite peaks varying in intensity under varying conditions of pressure of the gases but easily obtainable from a glow discharge of the kind employed in this experiment: N^+, N_{3-2}^+, O^+, N_2^+, O_2^+, O_3^+, SO_2^+ and $H_2SO_3^+$. (2) In addition to the simple ions noted above there appears a smear of complex ions of larger mass up to a molecular weight of 200. The number of these heavy ions is small but is greater in air than in the pure gases and becomes relatively larger at higher pressures where the ions

make several hundred collisions with neutral molecules in the drift space. The peaks which appear most often and most prominently correspond to ions of the following molecular weights: 56–64, 76, 80, 96, 108, 128, 140, 160, 168 and 200. (3) Negative ions do not appear in measureable quantities.

It seems likely that the heavier ions consist of such combinations of atoms and molecules as $2N_2^+$, $N_2O_2^+$, $2O_2^+$, $N_2O_3^+$, $O_2O_3^+$, $N_2O_5^+$ etc. The preliminary results obtained in these experiments do not definitely answer the question of the nature of gaseous ions. However, the fact that in air at higher pressures the heavier ions become nearly equal in number to the lighter ions indicates that after some aging air ions at least do not consist of simple atoms and molecules of nitrogen and oxygen, or even of ozone and N_3. In particular, nitric oxides probably play an important role in the formation of the heavier molecular aggregates. On the other hand, in pure oxygen and nitrogen, the relative number of heavy ions is much smaller even at high pressures and it is probable that aside from attachment to impurities the ions remain essentially of a simple nature. Undoubtedly O_3^+ and N_3^+ ions play considerable role in gas ion phenomena and apparently the O_3^+ ion is very stable while N_3^+ is less stable since it breaks up into $N_2^+ + N$ in the magnetic field. It is interesting to compare the behaviour of nitrogen and hydrogen. The writer as well as other observers employing a filament at low pressures (the order of 0.01 mm) has observed a considerable quantity of H_{3-1}^+ as well as H^+, H_2^+ and H_3^+. Apparently H_3^+ breaks up in the magnetic field into $H^+ + H_2$ while N_3^+ breaks up into $N_2^+ + N$.

There remains a point to be discussed regarding the possibility that certain heavy ions, if formed, would break up in the analyzing chamber where they are rapidly accelerated in electric and magnetic fields. If the ions are relatively stable it should be impossible for a breakup to occur as long as there is no collision with neutral molecules or other ions. Since this condition is fulfilled in a molecular beam of the type employed in these experiments, and a certain number of heavy ions have actually been observed, some of the ions at least are able apparently to withstand the shock of acceleration in the fields. On the other hand a breakup in the magnetic field is certainly observed in the case of N_3^+ and H_3^+. It seems doubtful however that this effect is due directly to the magnetic forces. An ion of this sort may be stable only when in an excited state and if radiation takes place a breakup may follow. The possibility remains that other less stable heavy ions may be present which have not been observed owing to a change of mass in the analyzing chamber. Perhaps the more or less irregular smear of heavy ions observed is due in part to an effect of this sort; but the important fact remains that ions up to a molecular weight of 200 have been observed, indicating that aged ions in air are of a complex and probably heterogeneous nature.

In conclusion, the writer wishes to take this opportunity for expressing his gratitude to Professor L. B. Loeb whose advice and help have been an inspiration throughout the course of these and previous experiments at the University of California. He also wishes to thank Professor Otto Stern of Hamburg for valuable suggestions in regard to the technique of molecular beams, and Commander T. Lucci of the Italian Navy, retired, who aided in taking some of the readings.

THE MOLECULAR SCATTERING OF LIGHT FROM AMORPHOUS AND CRYSTALLINE SOLIDS

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(Received September 22, 1931)

Abstract

There have been photographed the Raman spectra of several specimens of plate glass and of certain crystalline sulphates and their water solutions. In the case of the plate glass it is shown that at least most of the lines owe their origin to the silica content. The data for the crystalline sulphates are of interest because of the appearance of lines corresponding to both the active and inactive frequencies of the sulphate ion. These lines also make their appearance when the crystals are dissolved in water. With the data now available in the literature it is difficult to describe exactly the shifts of the Raman lines produced by the solution process because these shifts frequently depend upon the concentration of the ions and because for a given concentration different lines may be shifted by different amounts.

THE theoretical and experimental study of the Raman effect has justified the vast amount of work devoted to it, both as a means of demonstrating the quantum laws and as an analytical tool in probing the internal structure of chemical compounds. For the latter purpose it serves to study the structure of molecules either in the pure or dissolved state. In the hands of Kohlrausch[1] and of Andrews[2] and their associates there has been accumulated considerable information concerning the frequencies of and modes of vibration about the various kinds of chemical bonds in pure organic compounds. The Raman effect has also been used in a number of instances to study the structure of inorganic crystals and amorphous materials. Nisi,[3] Woodward,[4] Rao,[5] and a number of other investigators have used its study to indicate the changes taking place when an inorganic electrolyte is dissolved in water, it being predicted that in this manner there may eventually be obtained a quantitative measure of the degree of dissociation of the salt into ions. In general the work with inorganic substances and their solutions has not been as successful as that with the organic liquids and there remain many difficulties to be overcome.

The work to be reported in this article has to do with the molecular scattering of light from inorganic solids and from their water solutions in the cases where they are sufficiently soluble. The substances are in most cases crystalline in nature. Data for certain of these systems were presented more than two years ago as preliminary communications to this Journal.[6] It has just now

[1] Kohlrausch, "Der Smekal-Raman Effekt," Springer, Berlin, 1931.
[2] Andrews, *et al*, Phys. Rev. **36,** 531 (1930).
[3] Nisi, Jap. Jour. Phys. **5,** 119 (1929).
[4] Woodward, Phys. Zeits. **32,** 212 (1931).
[5] Rao, Proc. Roy. Soc., **A127,** 279 (1930).
[6] Hollaender and Williams, Phys. Rev. **34,** 380, 994 (1929).

been possible to improve the early results in accuracy and to make the proper identification of the excited line with its exciting line in several cases, where errors could not at that time be avoided, by means of improved apparatus and experimental methods which have since become available to us.

The experimental procedure differed scarcely if at all from that described by Kohlrausch[1] and by Schaefer and Matossi.[7] The salt solutions were placed in a long tube, illuminated along its length with a commercial mercury arc, and the spectrum of the light scattered at right angles was photographed by means of a large glass spectrograph through a plane window in the end of the tube. The tubes were cooled by means of a water jacket and the lamps were cooled by an electric fan. The measurements reported here were made with instruments manufactured by Steinheil. The tube containing the solutions was replaced by smooth flat sections of the solid when exposures of glasses and crystalline substances were made. A system of filter solutions was developed so that either of the exciting lines used (Hg 4047 or Hg 4358) and all other strong lines of the mercury arc could be so reduced in intensity that the systems were exposed to a radiation which was practically monochromatic. The filters used were acid solutions of quinine sulphate for the 4047 group and solutions of iodine in carbon tetrachloride for the 4358 group or for lines of longer wave-length. The plates were photometered with a Moll recording microphotometer, kindly placed at our disposal by the Department of Physics. The position of the Raman lines was also determined directly from the plates with a Gaertner comparator.

I. Raman Effect in Amorphous Solids

Infrared studies with crystalline materials have led to such interesting theoretical conclusions[8] that it is only natural for the Raman effect to have been discovered in these substances very shortly after the original announcement of Raman. Crystalline quartz has given a number of scattered lines whose frequency differences, but not intensities, agree quite well with those of infrared absorption and reflection maxima. The large number of observed frequencies is somewhat surprising because a single SiO_2 molecule can have not more than three characteristic frequencies and it can be explained only by assuming the crystal to have a very complicated lattice. One might expect to find even more scattered lines in fused quartz or in a glass containing a large percentage of silica because of a still more complicated structure. Furthermore, at the time of our original experiments it was believed that the Raman effect could not be observed in a fused quartz.[9] Exposures have been made with a number of samples of plate glass, the results of a typical experiment being given in Table I.

Gross and Romanova[10] and very recently Bhagavantam[11] have also reported successful exposures of fused quartz and various glasses. Their results

[7] Schaefer and Matossi, Fortschritte der Chemie, Physik u. phys. Chem. **20,** No. 6 (1930)

[8] See, for example, Schaefer and Matossi, "Das Ultrarote Spektrum," Springer, Berlin, 1930

[9] Pringsheim and Rosen, Zeits. f. Physik **50,** 741 (1928).

[10] Gross and Romanova, Zeits. f. Physik **55,** 744 (1929).

[11] Bhagavantam, Ind. Jour. of Phys. **6.** 1 (1931).

TABLE I. *Data for plate glass.*

Exciting line	Excited line	$\Delta\nu$	λ
4358	4718	1748	5.7
	4682	1585	6.3
	4619	1293	7.7
	4572*	1071	9.3
	4513	785	12.7
	4485	647	15.5
	4463	537	18.6
	4450	471	21.2
	4408	259	38.6

* This is the most intense band. The microphotograph indicates that it may possibly be resolved into three lines, with the most intense one in the center.

(in part) are compared with those of the authors in Table II. As far as the data now available in the literature are concerned the Raman spectra for both crystalline and fused quartz and for the various glasses are almost identical. Therefore, it is impossible to draw any conclusions with regard to the crystal structure, or lack of it, in these materials.

TABLE II. *Data for quartz and the glasses.*

Material	Reference	Frequency differences							
Crystalline quartz	10	125	264	463	526	633	800	1075	1220
Amorphous quartz	10	—	263	440	500	670	800 to 830	1030 to 1090	1240
Flint glass	11	119*	—	460 to 500	—	640	780	1080	1320
Crown glass	11	115*	340	460	—	650	800	1070	1320
Plate glass	†	—	259	471	537	647	785	1071	1293

† This article.
* Observed by Gross and Romanova.

In the glasses the scattering was extremely faint, and even when mirrors were used to concentrate the incident light upon the sample, exposures of from 3 to 10 days, depending upon the color of the sample, were required. The Raman lines were always more or less diffuse, rather than sharp as in the case of crystalline quartz, and it has been necessary to estimate the position of maximum intensity in order to measure their position. The comparison table indicates that at least most of the lines owed their origin to the silica content (SiO_2), in other words they were due to molecular vibrations characteristic of the constitutent materials.

The presence of the frequency differences 1748 and 1585 was somewhat surprising. These differences, corresponding to shorter wave-lengths, have not been observed in quartz. It is considered possible they may have resulted from the other constituents of the glass. To be certain of the existence of these larger frequency differences all mercury lines between 4358A and 5300A have been filtered out. For different samples of glass these larger frequency differences appear to change their position.

II. Raman Effect in Crystalline Sulphates and their Water Solutions

Two types of crystals may be distinguished, those with simple ions at the lattice points, and those containing complex ions. In the simple ion lattice one mode of vibration is possible, but in the complex crystals two kinds of vibration are known, a lattice or "outer" vibration in which, for example, the complex anion vibrates with respect to the metal ion, and an atomic or "inner" vibration in which the complex ion remains fixed in position and its individual atoms vibrate with respect to each other. Roughly speaking the frequencies of the inner vibrations will be independent of the particular cation present. They will also correspond to shorter infrared wave-lengths than those of the outer vibrations. It has been possible only in exceptional cases to find Raman lines corresponding to the outer vibrations, but this may be in part due to difficulty in obtaining optically clear crystals. Information concerning the inner vibrations of an ion may be obtained either from the crystals themselves or from their water solutions because only the lattice bonds are destroyed by the solvent.

There has been much discussion with respect to this particular point. Is there a shift in the characteristic frequency differences given by an ion when it is dissolved or are they unchanged? It is claimed by some investigators that smaller frequency differences (corresponding to longer wave-lengths) are found in solution while such shifts have not been evident in the data of others. From a theoretical point of view one can certainly expect to find these shifts. The experimental data now available in the literature seem hardly adequate to settle this point, the most important reason being that shifts due simply to changes in the concentration of the solutions have hardly been considered. In most cases the concentrations of the solutions studied have not been given. Recent data of Embirikos[12] are of interest in this connection because they show that in passing from a 1 normal solution to a 2 normal solution the frequency difference for Li_2SO_4 changed from 989 to 999 and for $MgSO_4$ it changed from 986 to 996. The presence of water of crystallization may also modify any changes in frequency difference due to the solution process.

Of the crystals containing complex ions the carbonates and sulphates have been most completely studied, but there still remain many difficulties to be overcome. In the case of the SO_4 ion infrared reflection maxima at 9μ and 16μ, corresponding to active frequencies, are known. There are also two inactive frequencies, one of which is, in all probability, given by the Raman frequency difference 980, corresponding to 10.2μ. The other has been calculated from these three to be about 26μ by Schaefer.[13]

Data, presented in Table III, have been obtained for the molecular scattering of light from crystalline gypsum, barium sulphate and copper sulphate, and from water solutions of copper sulphate, magnesium sulphate and potassium alum. The crystals used contained smaller amounts of impurities and

[12] Embirikos. Zeits. f. Physik **65,** 266 (1930).

[13] Schaefer, Zeits. f. Physik **60,** 586 (1930). See also reference 8, page 352.

TABLE III. *Data for crystalline sulphates and their water solutions.*

Exciting line	Excited line	$\Delta\nu$	λ	Remarks
		Gypsum ($CaSO_4 \cdot 2H_2O$)		
4358	4584	1128	8.9	
	4553	980	10.2	
	4495	696	14.3	
4047	4701	3437	2.9	Water band
	4613	3031	3.3	Water band
	4213	980	10.2	
		Barite ($BaSO_4$)		
4358	4553	980	10.2	
	4496	702	14.3	
	4448	461	21.6	
4047	4213	980	10.2	
		Copper sulphate ($CuSO_4 \cdot 5H_2O$)		
4358	4553	980	10.2	
4047	4701	3437	2.9	Water band
	4213	980	10.2	
		Copper sulphate, 1 normal water solution		
4358	4553	980	10.2	
	4477	607	16.5	
4047	4701	3437	2.9	Water band
	4651	3208	3.1	Water band
	4213	980	10.2	
	4169	723	13.7	
		Magnesium sulphate, 1 normal water solution		
	4584	1128	8.9	
4358	4553	980	10.2	
	4497	706	14.3	
	4477	607	16.5	
	4452	482	20.8	
		Potassium alum, saturated water solution at 25°C		
4358	4553	980	10.2	
	4477	607	16.5	
	4451	477	21.0	
4047	4213	980	10.2	

were imperfect in structure. The scattering produced by these imperfections made it impossible for us to observe some of the weaker lines reported by others.

Lines were found corresponding to the active frequencies 9μ and 16μ, and to the inactive frequencies 10μ and 26μ. The agreement with the longest wave-length, a calculated position, was not good. Thus for this wave-length, Schaefer, Matossi and Aderhold reported a Raman line corresponding to 24.5μ,[7] but later corrected it to 21.7μ. This Raman line in the work of Dickinson and

TABLE IV. *Data for substances containing SO_4 radical.*

Substance	Author	Frequency differences								
Sulphuric acid 100%	N	414	564	740	911	—	1043	1170	1366	1517
Sulphuric acid 100%	W	430	580	—	908	—	—	1143	1359	—
Ammonium sulphate solution	D-D	458	624	—	—	987	—	—	—	—
Copper sulphate	J-D	429	602	—	—	980	—	1091	—	—
Gypsum	S-M-A	460	620	—	—	985	—	1139	—	—
Gypsum	H-W	—	—	696	—	980	—	1128	—	—
Barite	H-W	461	—	702	—	980	—	—	—	—
Copper sulphate 1 N solution	H-W	—	607	723	—	980	—	—	—	—
Magnesium sulphate 1 N solution	H-W	482	607	706	—	980	—	1128	—	—
Alum solution	H-W	477	607	—	—	980	—	—	—	—

N Nisi, reference 3.
W Woodward, reference 4.
D-D Dickinson and Dillon, Proc. Nat. Acad. Sci. **15,** 334 (1929).
S-M-A Schaefer, Matossi and Aderhold, Zeits. f. Physik **65,** 289 (1930).
J-D Joos and Damaschun, Phys. Zeits. **32,** 553 (1931).
H-W This article.

Dillon corresponds to 21.8μ, that of Joos and Damaschun to 23.3μ, and those of the present authors average 21.0μ.

There have been collected in Table IV data for substances containing the SO_4 radical. No attempt has been made to include all the available data, its chief purpose is to show the order of agreement between values reported from different laboratories and to compare the interesting data of Nisi and of Woodward for pure sulphuric acid with those of the crystalline sulphates. In the data for pure sulphuric acid the frequency difference 980 does not appear, but when the solution has been diluted to 50 percent by volume with water there is no doubt concerning its presence. Woodward does not find the difference 1043 until a small amount of water is present and believes this frequency to be due to the HSO_4^- ion. The 980 frequency difference is assigned to the SO_4^{--} ion.

The effect of the presence of increasing amounts of water in the sulphuric acid is interesting in connection with a point already mentioned. Certain of the frequency differences are, within the limits of experimental error, perfectly constant throughout the whole range of concentration 100 percent sulphuric acid to 10 percent sulphuric acid by volume, several increase with dilution, and others decrease with dilution. These and other data indicate that no simple general statement will describe the effect of the solution process upon a characteristic frequency difference, they also explain why in certain cases no shift has appeared while in others there may be appreciable changes. The data of this article cannot be claimed to be sufficient to contribute to the solution of this particular problem. We have, however, been able to verify the magnitude of the shift of the line corresponding to the frequency difference 980 reported by Embirikos in the case of one and two normal water solutions of magnesium sulphate.

The frequency difference, approximately 700, has been found by us in gypsum, barite, and solutions of copper and magnesium sulphates, but has not been reported by other investigators, studying these same systems. Nisi has reported 740 for pure sulphuric acid. This difference corresponds to approximately 14μ, the position of a known infrared reflection maximum for water, but it is difficult to see how this Raman shift can be accounted for on the basis of the presence of water. We are at present unable to assign a definite significance to it.

As indicated in Table III frequency differences corresponding to wavelengths of the order of magnitude 3μ are to be associated either with the water of crystallization or with the solvent water. The water bands were also present in the spectrum of the magnesium sulphate solution but no attempt was made to locate their maximum intensities. The very exact study of the Raman effect in such systems as have been reported here promises to give information not only with regard to the dissociation process but also to clear up some of the difficulties which have been met in the study of the water bands themselves. There seems to be a tendency for the individual components of the latter to become sharper and more distinct as the concentration of the added electrolyte is increased.

AN INTERPRETATION OF THE SELECTIVE PHOTOELECTRIC EFFECT FROM TWO-COMPONENT CATHODES

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Abstract

Evidence is produced to support the view that photoelectrically selective, two component cathodic surfaces are crystalline in nature. Then, assuming that Fowler's equation for the energy of electrons selectively transmitted through a single potential valley $[W=(n^2h^2/8md^2)]$ is equally valid for the energy of electrons selectively transmitted through the periodic sequence of valleys characteristic of the potential field within a crystal, and that all of the energy of photoelectrons is acquired from the incident light quanta, the wave-lengths of light to which such a surface should respond selectively can be computed. Such computations have been made with d equal to the internuclear distance between electro-positive ions in the lattice structure of alkali metal hydride, oxide and sulphide crystals. The hydride crystals belong to the sodium chloride type and the oxide and sulphide crystals are supposedly of the calcium-fluoride type. The correlation between these computed values and the positions of the observed selective maxima is exceptionally good. Moreover, the fact that the alkali metal hydrides exhibit but one selective maximum and the oxides two or three maxima is in keeping with the geometry of their respective crystalline types.

ONE of the most significant characteristics of the photoelectric emission from two-component cathode surfaces, such as those of the alkali metal hydrides and oxides, is the selective response to light of specific frequencies. This results in the appearance of definitely located maxima in the spectral response curves for these compounds. To avoid the necessity of repeated reference to other publications, I have assembled a group of typical curves and present them in Fig. 1.

A number of ideas have been advanced to account for a selective response to light, but heretofore no theory has adequately explained why: (1) A single specifically located maximum is always observed in the spectral response curve of any given alkali metal hydride surface; (2) One, two or three definitely located maxima may appear in the spectral response curve of an alkali metal oxide cathode, depending presumably upon the relative proportions of metal and oxygen, and the technique involved in the preparation of the compound; (3) The wave-length of the light to which a two-component surface responds selectively is a direct function of the size of the components.

In this paper I propose an interpretation of the composition of two-component cathode surfaces, and an explanation of the selective photoelectric emission therefrom which accounts for all the above observations with striking precision.

Preparation of Two-Component Selective Photoelectric Surfaces

The preparation of light sensitive alkali metal hydride photoelectric cells,[1,2] as is quite generally known, consists in ionizing hydrogen by means of an electrical brush discharge, on a coating of freshly distilled metal. Possibly

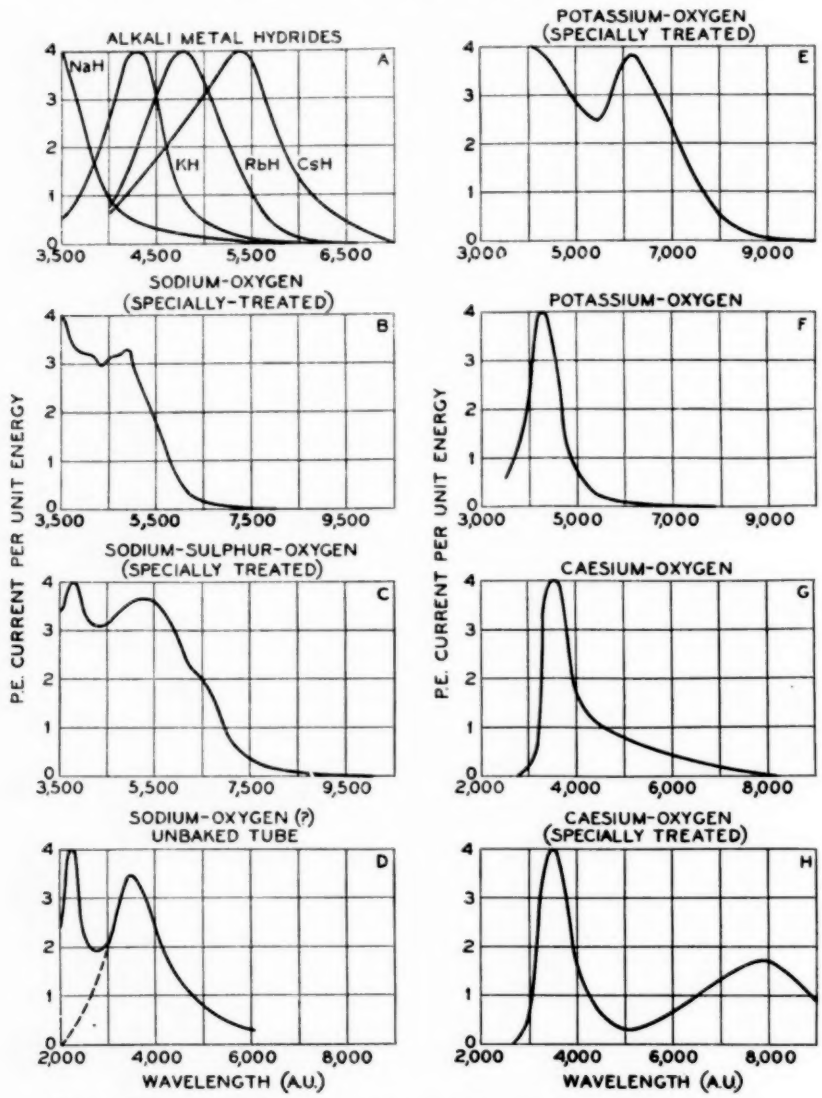

Fig. 1. Groups of typical spectral response curves for various gas-treated alkali metal photoelectric cells.

better results are obtained when the metal is made the cathode during the discharge, but this is not absolutely essential. Typical spectral response characteristics of such cells for visible light are shown in Fig. 1A.

[1] H. E. Ives, Bell System Tech. J. **5**, 320 (1926).
[2] E. F. Seiler, Astrophys. J. **52**, 3, 129 (1920).

The method of preparing selectively emitting cathodes of the alkali metals by the use of oxygen has been the subject of considerable experimentation in recent years. The mere introduction of small amounts of this gas onto an alkali metal surface is sufficient to greatly enhance the photoelectric sensitivity,[3] but in these cases the pronounced selective maxima in the spectral response curves appear, in general, at practically the same wave-lengths as those for the pure metals or the hydrides, as illustrated for the cases of sodium and potassium by the curves in Fig. 1D and 1F. However, if after oxidizing the surface of a sodium cathode, a limited area is heated to create a vapor of sodium and oxygen, a coating is formed on the cool portions of the cathode which is very much more sensitive to light and exhibits a quite different spectral response characteristic, with a new selective maximum at longer wave-lengths (Fig. 1B). Moreover, if on a silver plate which has been oxidized under control, caesium in the proper proportions is deposited and the whole sub-

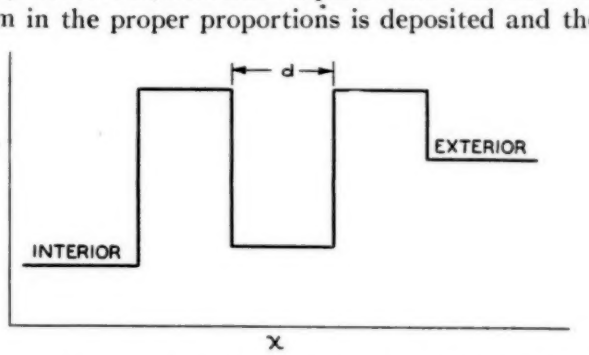

Fig. 2. Conventional representation of the work done by an electron in passing through a surface consisting of alternate layers of electropositive and electronegative elements, as Ag–O–Cs–O–Cs.

jected to a heat treatment which includes as a final step, heating to a temperature just under that at which caesium monoxide volatilizes (250°C),[4] a cathode strikingly sensitive to red and near infrared light is obtained (Fig. 1H).[5] By means of a similar process, red sensitive potassium-oxide photoelectric cells can also be made (Fig. 1E).[6] Obviously, the processes described above produce a complex surface structure, physically favorable to the emission of electrons by light. The nature of this structure and an explanation of these pronounced maxima are the subjects of this discussion.

Campbell-Fowler Theory

Campbell,[7] in an attempt to account for the selective response of caesium-oxide cells to red light, suggested that the surfaces of their cathodes consist of alternate layers of oxygen and caesium. The structure he mentioned as most

[3] A. R. Olpin, Phys. Rev. **36,** 251 (1930).

[4] J. W. Mellor—"A Comprehensive Treatise on Inorganic and Theoretical Chemistry." Vol. II p. 486. Longmans, Green and Co., Ltd., London (1927).

[5] L. R. Koller, Phys. Rev. **36,** 1639 (1930).

[6] N. R. Campbell, Phil. Mag. **6,** 633 (1928).

[7] N. R. Campbell, p. 10 "A Discussion on Photoelectric Cells and their Application"—The Physical and Optical Societies, London (1930).

likely was Ag–O–Cs–O–Cs. The potential energy of an electron moving through such a sequence of atomic or molecular layers was conventionally represented by a diagram similar to the one in Fig. 2, wherein the abscissa is the distance normal to the surface and the ordinate, the potential energy of a electron moving in this direction. Fowler[8] then showed, by means of the wave mechanics, that, to a first approximation, the transmission of electrons through such a surface structure will be greatest provided the waves associated with their motion are of such length that they will form stationary waves in the potential valley.

If the width of the valley is d, the condition for standing waves to form, obviously, is that

$$\lambda = \frac{2d}{n} \ (n = \text{an integer}). \tag{1}$$

But since the wave-length associated with a moving electron is

$$\lambda = h/mv, \tag{2}$$

according to Campbell and Fowler's theory, the speed of electrons most readily transmitted should be

$$v = \frac{nh}{2md}. \tag{3}$$

Consequently, the kinetic energy of such electrons will be

$$w = \tfrac{1}{2}mv^2 = \frac{n^2h^2}{8md^2}, \tag{4}$$

which is the expression Fowler obtained from a rigorous solution of Schroedinger's wave equation.

If all the energy possessed by the electron is acquired from the incident light quanta, then

$$w = \tfrac{1}{2}mv^2 = h\nu = \frac{n^2h^2}{8md^2} \tag{5}$$

and

$$\nu = \frac{n^2h}{8md^2}. \tag{6}$$

A hasty computation of this energy value when d is of atomic or molecular dimensions indicates that if it is to correspond to that of a quantum of visible or near infrared light, n must be unity. Eq. (6) is thus a simple relationship between the frequency of light ν for which maximum emission should occur and the width of the potential valley d responsible for this selectivity. Replacing ν by c/λ and simplifying, we get

$$d = 0.0551(\lambda_{max})^{1/2} \tag{7}$$

or

$$\lambda_{max} = 330.d^2, \tag{8}$$

where both λ_{max} and d are expressed in Angstrom units.

[8] R. H. Fowler, Roy. Soc. Lond. Proc. **A128,** 123 (1930).

More recently Frenkel,[9] while adhering to Fowler's idea of selective transmission, announced that a "selective transparence must exist for any type of surface field involving a transition of the potential energy from one (constant) level inside the metal to another constant level outside it irrespective of the presence or absence of local maxima or minima".

Nature of Compounds on Two-Component Cathode Surfaces

On account of the simplicity of the relationships expressed by Eq. (8), it would be easy to check Fowler's theory, were it possible to determine the proper value of d to use. Physically, the conventional distribution of potential showing a valley as diagrammed in Fig. 2 does not exist. Even though we concede the actual presence of alternate layers of electropositive and electronegative atoms or ions on the cathode surface, as postulated by Campbell, the potential energy of an electron passing through such a configuration must more nearly resemble that represented by the diagram in Fig. 3. Here

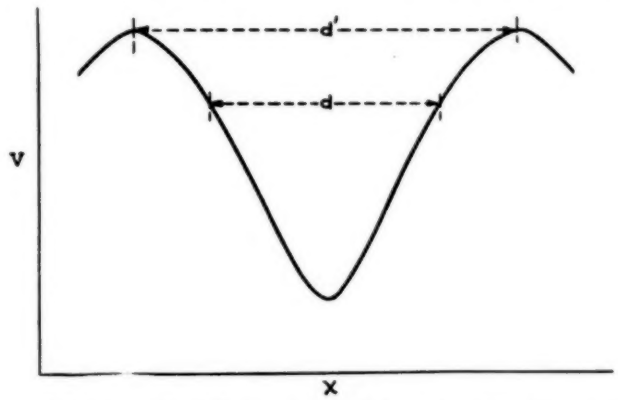

Fig. 3. Potential energy of an electron passing through a structure consising of a layer of electropositive ions sandwiched between layers of electronegative ions.

the width of the valley is a function of its depth, and consequently it is not easy to obtain a quantitative correlation between λ_{max} and d. We can, however, insert the observed values of λ_{max} in Eq. (7) and see whether or not the values of d called for, are of the order of magnitude of atomic dimensions. Actually, they are found to lie between 3 and 5 Angstroms, which suggests a very rough correlation with the atomic diameters of the alkali metals.

The values of d obtained by Eq. (7) when the observed values of λ_{max} for alkali metal surfaces sensitized with hydrogen are used, have been tabulated in Table I, and those obtained when the observed values of λ_{max} for alkali metal surfaces sensitized with oxygen are used are listed in Table II.

It will be noted that the values in the first table are very nearly equal to the sum of the diameters of the positive metal and negative hydrogen ions multiplied by $\frac{1}{2}(2)^{1/2}$, and those in the latter table are approximately equal to the sum of the diameters of the positive metal and negative oxygen ions multiplied by either $\frac{1}{3}(3)^{1/2}$, $\frac{1}{2}(2)^{1/2}$, or $\frac{1}{3}(6)^{1/2}$.

[9] J. Frenkel, Phys. Rev. **38**, 309 (1931).

TABLE I.

Cathode material	λ_{max} (observed)	$d=0.0551(\lambda_{max})^{1/2}$	d' = sum of diameters of positive metal and negative H ions[10]	$\frac{d}{d'}$
LiH	2800A	2.92A	4.10A	0.712
NaH	3300	3.17	4.50	.704
KH	4350	3.63	5.20	.698
RbH	4800	3.82	5.52	.692
CsH	5400	4.05	5.84	.694
				$[\frac{1}{2}(2)^{1/2}=0.707]$

TABLE II.

Cathode material	λ_{max} (observed)	$d=0.0551(\lambda_{max})^{1/2}$	d' = sum of diameters of positive metal and negative O ions[10]	$\frac{d}{d'}$
Sodium oxide	2270A	2.62A	4.60A	0.570
"	3500	3.26	4.60	.709
"	4700	3.78	4.60	.822
Potassium oxide	3130	3.08	5.30	.582
"	4260	3.57	5.30	.674
"	6200	4.34	5.30	.819
Caesium oxide	3500	3.26	5.94	.549
"	5500	4.09	5.94	.689
"	8000	4.93	5.94	.830
				$[\frac{1}{3}(3)^{1/2}=0.578;\ \frac{1}{2}(2)^{1/2}=0.707;\ \frac{1}{3}(6)^{1/2}=0.818]$

Obviously, these factors suggest a definite configuration or alignment of molecules on the surface in some form of cubical arrangement, which, in turn, suggests the presence of a crystalline formation on the gas-treated alkali metal cathodes of photoelectric cells, and the existence of selective maxima because of selective transmission of electrons through the periodic fields of potential characteristic of such structures. The nature and dimensions of the respective crystalline forms will be considered in greater detail in succeeding paragraphs.

An interpretation of the cathode surface as a crystalline arrangement of the component ions impresses us as a very reasonable picture, for the amount of material used in forming some of the best photoelectric cells indicates that the surface coatings of the cathode might be as thick as 1,000 atom diameters. Certainly, they are sufficiently thick to be plainly visible and they contribute a definite coloration to the surface. Now, the fact that it is the ratio of alkali metal to oxygen (approx. 3 to 1) and not the total amount of each that determines the selective characteristic of a surface,[11] together with the fact that the final heat treatment previously described is of such a nature that the molecules deposited on the cathode will be thermally agitated but not evaporated, suggest strongly the likelihood of a crystalline formation. At the same time

[10] See Table of Ionic Radii, V. M. Goldschmidt, Far. Soc. Trans. **25,** 6, 253 (1929).

[11] This is based on an unpublished report by Dr. C. H. Prescott of the Bell Telephone Laboratories after considerable experimentation. A recent paper by N. R. Campbell [Phil. Mag. **12,** 75, 173 (1931)] further substantiates this ratio.

any excess free alkali metal, having a lower boiling point than the salt, will deposit on the top surface of the crystal and greatly reduce the work function.

A crystalline surface structure will exhibit a periodic succession of potential valleys instead of a single potential valley as postulated by Campbell and Fowler. Just how this condition will affect the validity of Eqs. (4) to (8) has not yet been investigated. However, I shall proceed to point out a striking correlation between observed positions of selective maxima and those computed by means of Eq. (8) when values of d associated with the period of the potential field in a crystal are used.

Alkali Metal Hydrides

All of the alkali metal hydrides are known to crystallize with the sodium chloride structure.[12] The arrangement of ions in a unit cell of this type is diagrammatically shown in Fig. 4.

The most likely path for an electron to follow in passing through such a crystal is one normal to the 110 plane and quite close to the positive metal

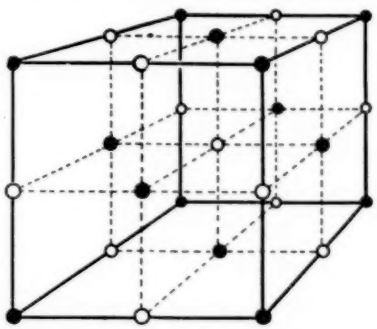

Fig. 4. Arrangement of ions in alkali metal hydride crystals (NaCl structure). The circles represent the metal and the dots the hydrogen ions.

ions. In any other direction through the crystal, an electron will encounter more powerful retarding potentials because of the presence of negative hydrogen ions along its path. The nature of the potential field normal to the 110 plane, that is, the work an electron must do in passing through a hydride crystal in this direction, has been computed by Mr. L. A. MacColl of these laboratories on the basis of certain simple assumptions as to the nature of the potential fields of atoms and ions. His results are illustrated by the curve in Fig. 5. The potential is periodic and the period is $\frac{1}{2}(2)^{1/2}$ $(=0.707)$ times the sum of the diameters of the positive alkali metal and negative hydrogen ions. As illustrated in Table I, this is very close to the value of d, which when used in Eq. (8) gives values of λ_{max} in striking agreement with those observed. The fact that small deviations from the value 0.707 are noted for the hydrides of the more electropositive metals is likely due to the fact that Goldschmidt's values for ionic radii may not be altogether proper, since, as Bode[12] points out, the hydrogen ion is probably greatly deformed in the alkali metal hydrides, as indicated by the large refractive indices.

[12] H. Bode, Zeits. f. phys. Chem. (B) **6**, 251 (1930).

Alkali Metal Oxides

Whenever small amounts of oxygen or air come in contact with a clean alkali metal surface in an evacuated tube, the photoelectric sensitivity is greatly enhanced and a selective response to light of certain specific wavelengths produced.[13] In such cases a chemical reaction almost invariably occurs and it is usually of sufficient intensity that the heat of reaction might conceivably create a vapor pressure of the metal, so that a thin metallic film will deposit on the surface. Presumably, the compound formed by the chemical reaction and deposited underneath the metallic film is either the monoxide or peroxide of the metal. Similar compounds might be obtained by heating to high temperatures an oxidized silver or copper plate in the presence of the more reactive alkali metals, like caesium.

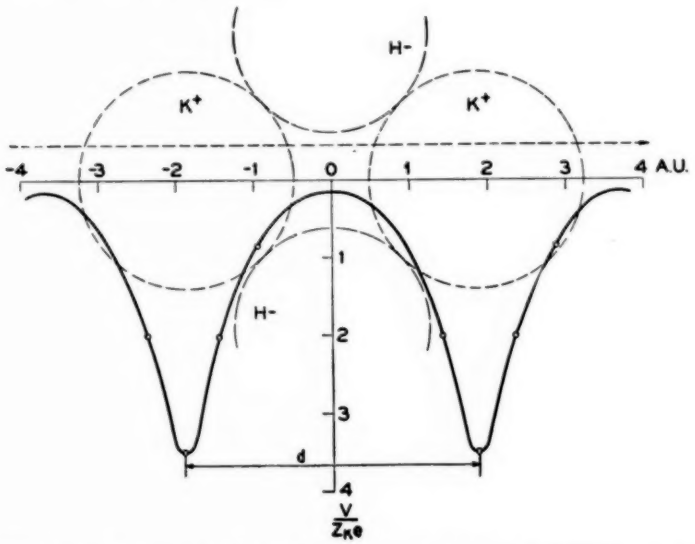

Fig. 5. The potential energy of an electron moving through a potassium-hydride crystal in a direction normal to the 110 plane, and at a distance from the nuclei of the potassium ions indicated by the dotted line with the arrowhead, can be represented by a periodic sequence of hills and valleys like the one shown here.

The selective transmission of electrons through surfaces coated with oxide films will be dependent upon the arrangement of ions in the individual molecules to a large extent. Adopting Slater's conclusions[14] that the valence bonds of the oxygen atom are mutually perpendicular, the diagrams in Fig. 6 representing caesium monoxide and sodium and caesium peroxide have been prepared. Obviously, an electron passing through such a surface structure will encounter a periodic field of potential and the period in the case of the monoxide will be $\frac{1}{2}(2)^{1/2}$ times the sum of the diameters of the metal and oxygen ions. In the case of the peroxide, the period is equal to the diameter of the larger ion in the molecule. More specifically, it is the diameter of the alkali

[13] A. R. Olpin, reference 3.

[14] J. C. Slater, Phys. Rev. **37**, 481 (1931).

metal ion in all cases excepting those of sodium and lithium cells; in the latter cases it must be the diameter of the negative oxygen ion.

These dimensions correlate closely with the value of d demanded by Eq. (8). The chief discrepancy comes in the case of the monoxide of the heavier metals, and this may result from the fact that the angle between the valence bonds in alkali metal monoxides is slightly greater than 90°. As a matter of fact Pauling[15] said it should be between 90° and 109°28′ but closer to the former value. Actually 95° will give the proper value of d to correlate the calculated and observed positions of the selective maxima. Or, this slight discrepancy may result from a number of other causes, such for example, as ionic deformation or selective light absorption. It is not the fact that there are slight discrepancies that is surprising, but rather the fact that they are so few and small.

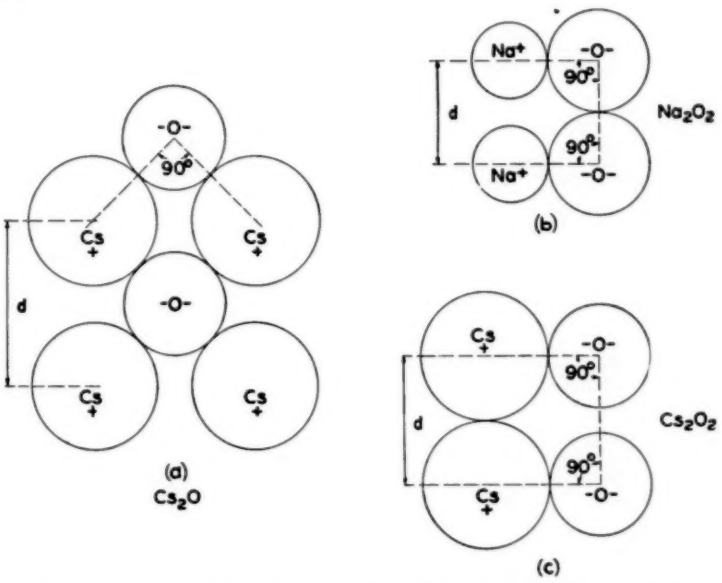

Fig. 6. Diagrams of molecular configurations illustrating distance of closest approach of component positive ions. (a) caesium monoxide, (b) sodium peroxide, and (c) caesium peroxide.

Whenever, as described previously, a cathode coated with an alkali metal oxide is heated under control in such a way that the surface molecules are agitated but not evaporated, and then the surface cooled rather quickly, the characteristic spectral response of the surface changes decidedly. Where there was a spectral maximum previously ,there now appears a minimum, and new maxima appear at other wave-lengths. Presumably this is due to a rearrangement of the ions or molecules on the surface into a crystalline structure.

The crystalline structure of the oxides of the alkali metals of large radii

[15] L. Pauling, J. A. C. S. **53,** 1356 (1931).
[16] Bijvoet and Karssen, Recueil des Travaux Chimiques des Pays—Bas **43,** 680 (1924).
[17] Claasen, Recueil des Travaux Chimiques des Pays—Bas **44,** 790 (1925).

has not been reported, but I have assumed that the monoxides have structures identical with those of Li_2O[16] and Na_2S.[17] In Fig. 7 the arrangement of ions in such a crystal is diagrammatically illustrated. Because of the nature of electrostatic forces within such a crystal, an electron transmitted through it will tend to follow a path close to the nuclei of the positive metal ions and normal to the 100 or 110 planes. The work it must do at various points along either of these paths can be represented by curves similar to the one in Fig. 5, which means that the electron encounters a periodic field of potential within the crystal. In the direction normal to the 100 plane the period is $\frac{1}{3}(3)^{1/2}$ times the sum of the diameters of the positive metal and negative oxygen ions, and in the direction normal to the 110 plane, the period is $\frac{1}{3}(6)^{1/2}$ times this sum. These are the values which must be used for d to satisfy Eq. (8) when the observed positions of the selective maxima are used, as shown in Table II.

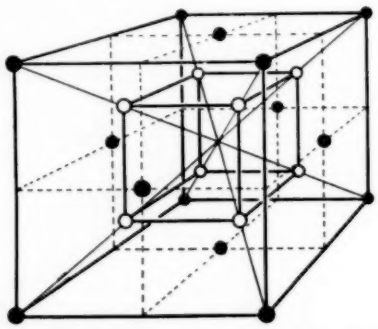

Fig. 7. Arrangement of ions in alkali metal monoxide crystals (CaF_2 structure). The circles represent the metal and the dots the oxygen ions.

Alkali Metal Sulphides and Other Compounds

In the light of the foregoing discussion, it is natural to expect that the wave-lengths of light to which an alkali metal sulphide responds selectively should be longer than for the corresponding oxide. Similarly, the selective maximum might be expected to appear at longer wave-lengths for selenides than for sulphides, and at still longer wave-lengths for tellurides as compared with selenides. Actually this condition has been qualitively observed in the cases of potassium-oxides, sulphides, selenides and tellurides,[18] and to some extent in the case of corresponding sodium compounds.[19] Also, I have recently obtained a good set of curves showing that the position of the selective maximum for the potassium halides is a function of the size of the halogen ion.

Since, in the preparation of the potassium sulphide photoelectric cells referred to in the preceding paragraph, no attempt is made to produce a crystalline arrangement of the surface ions, the separation of the positive ions undoubtedly is that determined by their positions in separate sulphide molecules; and the determination of this value will be similar to that used for the noncrystalline oxides. If the angle between the valence bonds in alkali metal

[18] W. Kluge, Zeits. f. Physik **67**, 497 (1931).

[19] A. R. Olpin, reference 3.

sulphides be taken as 90° and the surface coating be similar to that illustrated in Fig. 6 (a), the period of the resulting periodic field of potential is almost exactly the value of d called for by Eq. (8) in the light of experimental data.

When a sulphur-treated sodium photoelectric cell is subjected to treatment similar to that which supposedly forms a crystalline oxide surface, the selective maximum in the spectral response curve always appears at longer wave-lengths than is the case without the sulphur. Moreover, a small hump or irregularity is frequently observed in the spectral response curve at λ6500, where a maximum should appear for crystalline sodium sulphide, if it crystallizes with the calcium-fluoride structure (see Fig. 1C).

TABLE III.

Cathode material		Sum of diameters of metal and gas ions d'	d $(=\frac{1}{2}(2)^{1/2}d')$	λ_{max} $(=330.d^2)$	λ_{max} (observed)	Observer
LiH		4.10A	2.9A	2770	2800	Pohl and Pringsheim[20]
					3400	Pohl and Pringsheim[20]
NaH		4.50	3.18	3340	3300	Olpin and Briggs[21]
KH		5.20	3.68	4470	4350	Pohl and Pringsheim[20]
RbH		5.52	3.9	5020	4800	Pohl and Pringsheim[20]
CsH		5.84	4.13	5630	5400	Seiler[22]
Na_2O		4.60	3.25	3480	3500	Olpin[23] Richardson and Compton[24]
						Kluge[25]
K_2O		5.30	3.75	4640	4000–4600	Olpin[23]
Cs_2O		5.94	4.20	5820	5400	Pohl and Pringsheim[20]
						Olpin[23]
	non-crystalline		d(=diameter of O ion)			
Na_2O_2	non-crystalline		2.64	2300	2270	Richardson and Compton[24]
	non-crystalline		d(=diameter of metal ion)			
Cs_2O_2	non-crystalline		3.30	3590	3500	Koller[26]
			$d(=\frac{1}{2}(3)^{1/2}d')$			
Na_2O	crystalline	4.60	2.65	2320	2270	Richardson and Compton[24]
K_2O	crystalline	5.30	3.06	3090	3130	Wiedmann[27]
Co_2O	crystalline	5.94	3.43	3880	3500	Koller[26]
			$d(=\frac{1}{2}(6)^{1/2}d')$			
Na_2O	crystalline	4.60	3.76	4670	4700	Olpin[23]
K_2O	crystalline	5.30	4.33	6190	6200	Olpin[23]
Cs_2O	crystalline	5.94	4.85	7760	7500–8000	Koller[26] Zworykin[28]
						Olpin[23] Ballard[29]
			$d(=\frac{1}{2}(2)^{1/2}d')$			
Na_2S	crystalline	5.44	3.84	4860	4900	Olpin[23]
K_2S	crystalline	6.14	4.34	6200	6000–6200	Olpin[23]
	non-crystalline		d(=diameter of sulphur ion)			
Na_2S_2	non-crystalline		3.48	4000	3800	Olpin[23]
K_2S_2	non-crystalline		3.48	4000	4100	Kluge[25]
						Olpin[23]
			$d(=\frac{1}{2}(6)^{1/2}d')$			
Na_2S (Crystalline)		5.44	4.44	6500	6500	Olpin[23]

[20] R. Pohl and P. Pringsheim, "Die Liehtelektrischen Eischeinungen" Sammlung Viewig, Berlin (1914).

[21] A. R. Olpin and H. B. Briggs, unpublished.

[22] E. F. Seiler, reference 2.

[23] A. R. Olpin, reference 3.

[24] O. W. Richardson and K. T. Compton, Phil. Mag. **26,** 549 (1913).

[25] W. Kluge, reference 18.

[26] L. R. Koller, reference 5.

[27] G. Wiedmann and W. Hallwachs, Verh. d. D. phys. Ges. **16,** 107 (1914).

[28] V. K. Zworykin and E. D. Wilson, "Photocells and Their Application," p. 57.—John Wiley and Sons, N. Y. (1930).

[29] J. W. Ballard, J. O. S. A. **20,** 11, 618 (1930).

It appears, then, that the secret of making selective cathodes in photoelectric cells is that of forming a surface structure in which there is a periodic field of potential. If the selective reponse is desired at long wave-lengths, a large period is required; if at short wave-lengths, a small period. Of course, the surface work function is the limiting factor, however, for it is important that electrons transmitted or conducted through the periodic potential field can be emitted from the surface. In order to keep the work function as low as possible, a monoatomic film of electropositive metal is deposited on the surface.

In Table III are listed the values of d computed from the postulated surface structures described above, and the positions of the selective maxima given by Eq. (8) when these values are used. Opposite these computed values of λ_{max} are recorded the observed values and the observer.

The Lindemann Formula

In 1911 F. A. Lindemann[30] derived the following expression for the natural period of a vibrating system composed of two interpenetrating spheres of radius r and continuously distributed charge $\pm ne$ and $\pm e$ respectively:

$$\nu = \frac{1}{2\pi}\left(\frac{ne^2}{mr^3}\right)^{1/2} \tag{9}$$

This frequency, which is also the frequency of an electron revolving around a central body of charge $+ne$, was identified with that of the selective photoelectric maximum. Putting n equal to unity, the valence of the normal alkali metal atom, and r equal to the radius of each monovalent alkali metal atom in turn, values of ν are obtained in striking agreement with the observed frequencies for the metals and their hydrides.

More recently I pointed out[31] that if the several maxima, characteristic of oxide cells, result from the formation of different compounds, then all that is necessary to obtain values of ν by the Lindemann formula equivalent to the observed selective maximum is to assign to n the valence of the metal in those compounds. In this way the ultraviolet peaks in the response curves were ascribed to the peroxides (as Na_2O_2) of valence 2 and the maxima at long wave-lengths were ascribed to suboxides of valence 1/2 (as Na_4O). Although it is inconsistent with modern theory to think of a nuclear charge equal to $\frac{1}{2}e$ it was suggested that the force exerted on an electron by surrounding atoms might give that net effect.

By the Lindemann formula

$$\nu = \frac{1}{2\pi}\left(\frac{ne^2}{mr^3}\right)^{1/2}$$

and by the Fowler equation,

$$\nu = \frac{h}{8md^2}. \tag{10}$$

[30] F. A. Lindemann, Verh. d. D. phys. Ges. **13,** 482 (1911); ibid. **13,** 1107 (1911).

[31] A. R. Olpin, reference 3.

Equating these two expressions for the natural frequency of electronic systems,

$$\frac{1}{2\pi}(ne^2/mr^3)^{1/2} = \frac{h}{8md^2}, \tag{11}$$

or, simplifying,

$$d^2n^{1/2} = kr^{3/2} \quad (k = \text{const.}) \tag{12}$$

Now for any given metal atom r is constant, so that

$$d^2n^{1/2} = \text{a constant} \tag{13}$$

and d^2 varies inversely as $n^{1/2}$ or the square root of the valency.

As a specific case of this, take the case of the oxides of potassium. Eq. (13) becomes

$$d^2n^{1/2} = 9.12A^2, \tag{14}$$

when the radius of the potassium atom for coordination number 12 is used. By substituting the values of d computed from the structure of the surface compounds as described above [i.e. the sum of the diameters of the positive potassium and negative oxygen ions multiplied by $\frac{1}{3}(3)^{1/2}$, $\frac{1}{2}(2)^{1/2}$, and $\frac{1}{3}(6)^{1/2}$ respectively], the following values of n are obtained: $n=1.98$; $n=0.88$; $n=0.49$.

Similar values are found for the other alkali metals. These compare favorably with the values 2, 1 and 0.5 used as the valence of the alkali metal as mentioned above, and account for the generally close correlation between the experimentally observed positions of the selective maxima and those computed by either the Lindemann formula or the wave mechanics.

Summary and Conclusions

A theory of the selective photoelectric effect for gas-treated alkali metal cells is presented, based on the calculations of wave mechanics, the main features of which are: (1) A two-component cathodic surface structure within which there is a periodic field of potential; (2) Selective transmission of electrons through this field provided their energy bears a definite, fixed relation to its period; (3) Emission of electrons arriving at the surface provided the surface work function is sufficiently low.

A periodic field of potential is shown to be typical of that within a crystal, and a microcrystalline surface structure is postulated for all red-sensitive photoelectric cathodes.

Data are presented correlating the positions of selective maxima in observed photoelectric response curve for the alkali metal hydrides with the sodium chloride arrangement of ions, and the alkali metal oxides and sulphides with the calcium fluoride structure.

The single selective maximum observed in the spectral response of each hydride cell, and the several maxima characteristic of oxides and sulphides are shown to be the natural consequences of these structures.

A correlation between data heretofore obtained by the modified Lindemann formula and those obtained by the wave mechanics is explained.

ON THE THEORETICAL REQUIREMENTS FOR A PERIODIC BEHAVIOUR OF THE UNIVERSE

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(Received September 18, 1931)

Abstract

This article investigates, on the basis of relativistic mechanics and relativistic thermodynamics, the theoretical requirements for nonstatic models of the universe to exhibit a behaviour which is periodic in time. The discussion is limited to models which can be regarded from a large-scale point of view as filled with a uniform distribution of fluid, and the time coordinate is purposely chosen so as to agree with the proper time that would be used by local observers at rest in this fluid. It is first shown that the analytical requirements which would correspond to the continuous expansion and contraction of such models between definite maximum and minimum limits, together with the thermodynamic requirement that the expansion and contraction must be reversible, could not both be simultaneously satisfied with any fluid for filling the model which has reasonable properties. Attention is then turned to models of the universe having line elements which would be quasi-periodic in the time. A wide range of possibilities is found for models which would expand from zero proper volume to a maximum and then return, the treatment failing however to provide the analytical conditions for a minimum at the lower limit. It is pointed out, nevertheless, that from a physical point of view contraction to zero proper volume could only be followed by renewed expansion, so that we might expect for such models a continued series of expansions and contractions. Furthermore, it is found possible to satisfy the analytical requirements for such quasi-periodic behaviour by models which would expand and contract at a finite rate reversibly without increase in entropy, so that we might then expect a continued series of *identical* expansions and contractions. It is pointed out that Einstein's recent model of a nonstatic universe filled with incoherent matter, exerting no pressure and unaccompanied by radiation, would satisfy the thermodynamic as well as the analytical requirements for such a series of identical repetitions, and models filled solely with black-body radiation and with an equilibrium mixture of radiation and perfect gas are discussed which also satisfy these requirements. In conclusion some remarks are made concerning the bearing of such findings on the behaviour of the actual universe.

§1. Introduction

THE problem of the ultimate fate of our physical surroundings has long been the subject of human thought and speculation. *A priori*, three general types of future behaviour of the universe as a whole would appear to be possible. First, the universe might permanently remain in an approximately steady state; second, it might be subject to progressive change in some particular direction; and third, it might undergo a periodic change in properties, returning at definite intervals at least approximately to an earlier condition.[1]

[1] Different combinations of these general types of behaviour would of course also be possible. Thus we might have periodic happenings taking place simultaneously in different parts of the universe so related as to assure a steady state for the universe looked at as a whole. Or we might have a quasi-periodic behaviour superimposed on a general progressive change in a particular direction.

The possibility for the universe to be in an approximately steady state has usually been regarded as untenable, on account of the implications of the second law of thermodynamics and the actual observation of such important unidirectional phenomena as the flow of radiation from the stars. But interesting suggestions as to compensatory processes, which might really be maintaining the universe in a steady state, have sometimes been made.[2]

The second possibility of a progressive change in the properties of the universe in a particular direction, that of maximum entropy, has usually been regarded in the past as a necessary consequence of the second law of thermodynamics and has furnished what may be called the orthodox view of physics. This view might carry with it, however, the unsatisfactory implication that the universe was created with a supply of available energy at a finite time in the past. Moreover, the apparent inevitability of the view as a necessary consequence of the second law is diminished both by the possibility of fluctuations away from the maximum of entropy discovered many years ago by Boltzmann,[3] and by the previously unsuspected possibility for thermodynamic changes to take place at a finite rate without increase in entropy, which I have recently shown[4,5] to be allowed by the second law of thermodynamics in the form which it assumes in the extension of thermodynamics to general relativity.[6]

The third possibility, that the universe might be subject to a regular periodic change in properties, will be discussed in the present paper. This alternative has been discarded in the past since the classical form of the second law of thermodynamics would permit thermodynamic changes to take place in the universe at a finite rate only in the direction of increasing entropy, thus preventing any return of the universe to an earlier condition. It has now been demonstrated, however, that the relativistic form of the second law of thermodynamics would permit important changes to take place at a finite rate entirely reversibly without any increase in entropy at all. Thus in the case of a model of the universe filled solely with radiation, I have shown[4] that a reversible expansion of the universe could take place at a finite rate without increase in entropy, and that this expansion would be accompanied by a number of phenomena, such as the flow of radiation away from any given observer out into space, which would previously have been regarded as necessarily irreversible. And in the case of a model filled with a mixture of perfect gas and radiation, under the subsidiary assumption that the matter maintains

[2] See for example MacMillan, Astrophys. J. **48,** 35 (1919); Science **62,** 63, 96, 121 (1925); Millikan and Cameron, Proc. Nat. Acad. **14,** 637 (1928); Millikan, Nature **126,** 14 (1930).

[3] Boltzmann, Wied. Ann. **60,** 392 (1897).

[4] Tolman, Phys. Rev. **37,** 1639 (1931).

[5] Tolman, Phys. Rev. **38,** 797 (1931).

[6] The principles for extending thermodynamics to general relativity were developed in previous papers:—Tolman, Proc. Nat. Acad. **14,** 268 (1928); ibid. **14,** 701 (1928); Phys. Rev. **35,** 875 (1930); ibid. **35,** 896 (1930); and have been applied to problems of a different character than the present in other papers:—Tolman, Proc. Nat. Acad. **14,** 348 (1928); ibid. **14,** 353 (1928); ibid. **17,** 153 (1931); Phys. Rev. **35,** 904 (1930); Tolman and Ehrenfest, Phys. Rev. **36,** 1791 (1930).

itself in equilibrium with the radiation, I have been able to show[5] that a reversible transformation of matter into radiation could take place, and would be accompanied by a reversible expansion and reversible flow of radiation out into space.

Such examples of reversible changes make it very interesting to investigate the occurrence of models of the universe which would exhibit periodic behaviour, since such would now appear thermodynamically possible. It was pointed out, nevertheless, in the articles cited that neither of the above models would actually furnish a strictly periodic solution of the equations of motion, and this will be confirmed by more general considerations in the present article. Recently, however, a simple model of the universe has been discussed by Einstein[7] which exhibits a possibility for quasi-periodic solutions of a type which must now also be considered.

§2. Outline of Present Article

The discussion in the present article will be limited to models in which the universe can be regarded from a large-scale point of view as filled with a perfect fluid, having properties which change with the time but are independent of position. Furthermore, the time coordinate will be chosen so as to agree with the proper time as used by local observers at rest with respect to the material in the model, since it is evident that equations periodic in form with respect to an arbitrarily chosen time coordinate might have no special physical interest.

The possibilities for change with time in such models consist in an expansion or contraction in the proper volume of the universe. The equations of motion for such changes will first be obtained from the principles of relativistic mechanics, and the analytical requirement for these equations to correspond to a periodic expansion and contraction will be exhibited. Combining this analytical requirement with the thermodynamic requirement for periodic behaviour, namely that the motion should be reversible in the sense of relativistic thermodynamics, it will then be shown that no strictly periodic solution for the equations of motion would be possible for a model of this kind filled with any combination of incoherent matter and radiation. This general result confirms the conclusion already found for the two special models mentioned above, and also has the consequence of ruling out as physically probable the very interesting periodic line element recently proposed by Takéuchi.[8]

At first sight the result would appear to prove conclusively that no model whatever of the kind considered could exhibit a continued sequence of identical expansions and contractions. It will next be shown, however, that a new method of attack can be undertaken, by abandoning the attempt to find strictly periodic solutions of the equations of motion and considering instead quasi-periodic solutions which correspond to an expansion of the universe from zero proper volume to an upper limit and contraction again to the

[7] Einstein, Berl. Ber. (1931) p. 235. See also de Sitter, Bull. Astron. Inst. Netherlands **6**, 141 (1931).

[8] Takéuchi, Proc. Phys. Math. Soc. Japan **13**, 166 (1931).

starting point, the analytical treatment failing however outside the range between these points of zero volume.

A wide range of possibilities for solutions of this type will be found to exist. Furthermore, cases will be found where the analytical requirements for these quasi-periodic solutions can be satisfied by systems which expand and contract reversibly without increase in entropy. In such cases, since the only physical possibility after contraction to zero volume would be another expansion, and since the system arrives at the point of zero volume after contraction with unchanged entropy, it would seem allowable to expect a continued sequence of identical expansions and contractions, even though the mathematical analysis fails to carry us through the exceptional point of zero volume.

As mentioned above, one quasi-periodic solution corresponding to expansion from zero volume to an upper limit and return has already been given by Einstein.[7] It corresponds to a model in which the contents of the universe are taken as incoherent matter exerting zero pressure and unaccompanied by radiation. In this article it will be specially pointed out that the expansion and contraction of the Einstein model would not be accompanied by increase in entropy and hence could presumably be repeated over and over again.

Since the actual universe presumably contains radiation as well as matter, it will also be interesting to consider a model filled solely with black-body radiation which is the opposite extreme to the Einstein model containing nothing but matter. The form of line element for such a model will be exhibited, and it will be shown that this model would also expand and contract reversibly. Attention will then be turned to a more complicated model containing an equilibrium mixture of black-body radiation and perfect monatomic gas, and it will be shown that such a model could also furnish quasi-periodic solutions corresponding to reversible expansions and contractions. Finally in conclusion, a few remarks will be made concerning the possible bearing of such considerations on the problem of the behaviour of the actual universe.

§ 3. The Mechanics of the Nonstatic Universe

The line element for a nonstatic universe filled with a uniform distribution of matter and energy can be derived,[9] by treating the contents of the universe for the purposes of large-scale considerations as a perfect fluid, and written in the form

$$ds^2 = -\frac{e^{g(t)}}{[1 + r^2/4R^2]^2}(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2) + dt^2 \qquad (1)$$

where r, θ and ϕ are the spatial coordinates, t is the time coordinate, R is a constant, and the dependence of the line element on the time is given by the exponent $g(t)$.

With this choice of coordinates, particles which are at rest in the coordinate system will not be subject to acceleration but will remain perman-

[9] See Tolman, Proc. Nat. Acad. **16**, 320 (1930).

ently at rest, and it will be noted that the time coordinate t will agree with the proper time as used by local observers at rest with respect to such particles.

The proper pressure p_0 and proper macroscopic density ρ_{00} of the fluid corresponding to this line element are given by the equations[10]

$$8\pi p_0 = -\frac{1}{R^2}e^{-g} - \ddot{g} - \tfrac{3}{4}\dot{g}^2 + \Lambda \tag{2}$$

$$8\pi\rho_{00} = \frac{3}{R^2}e^{-g} + \tfrac{3}{4}\dot{g}^2 - \Lambda \tag{3}$$

where Λ is the cosmological constant. The pressure and density are independent of position, and are dependent as shown on the exponent g and its time derivatives $\dot{g}$ and $\ddot{g}$, and thus on the time itself.

The proper volume associated with the coordinate range $\delta r\ \delta\theta\ \delta\phi$ in accordance with the above line element, is evidently

$$\delta V_0 = \frac{r^2 \sin\theta\, e^{3g/2}}{\left[1 + r^2/4R^2\right]^3}\,\delta r\,\delta\theta\,\delta\phi \tag{4}$$

and since the dependence of the line element on the time occurs solely because of the functional dependence of the exponent g on t, it is evident that changes in the state of the universe with time can be characterized as expansions or contractions in proper volume, according as g is increasing or decreasing with the time.

In accordance with the expressions for pressure and density given by (2) and (3), this change in volume of the universe is governed by the simple equation[11]

$$\frac{d}{dt}\left(\rho_{00}\, e^{3g/2}\right) + p_0 \frac{d}{dt}\left(e^{3g/2}\right) = 0. \tag{5}$$

Or noting Eq. (4), we can write

$$\frac{d}{dt}\left(\rho_{00}\,\delta V_0\right) + p_0 \frac{d}{dt}\left(\delta V_0\right) = 0 \tag{6}$$

which shows that the change in the energy content associated with any small element of fluid is equal to the negative of the work performed on the surroundings.

§ 4. The Analytical Requirements for a Strictly Periodic Solution

Since changes in the line element with time occur because of the dependence of g on t, it is evident that the conditions for a strictly periodic behaviour of the model can be met only if g passes periodically through its minimum and maximum values. Using the subscripts 1 and 2 to denote the values assumed by different quantities when g has its minimum and maximum values, we can write as the analytical condition for the minimum

[10] See preceding reference, Eqs. (34).

[11] See Tolman, Proc. Nat. Acad. **16,** 409 (1930); Eq. (4).

$$g = g_1 \qquad \dot{g}_1 = 0 \qquad \ddot{g}_1 \geqq 0 \tag{7}$$

and as the condition for the maximum

$$g = g_2 \qquad \dot{g}_2 = 0 \qquad \ddot{g}_2 \leqq 0 \tag{8}$$

and by intercombination these expressions give as a necessary requirement for a strictly periodic solution

$$g_1 < g_2 \qquad \dot{g}_1 = \dot{g}_2 = 0 \qquad \ddot{g}_1 \geqq \ddot{g}_2 \tag{9}$$

§ 5. The Thermodynamic Requirements for a Strictly Periodic Solution

As the thermodynamic requirement for a strictly periodic solution, it is evident that the changes taking place in our model of the universe must be thermodynamically reversible, since otherwise it would not be possible for the model to return to an earlier state. As previously shown[12] in accordance with the principles of relativistic thermodynamics, the condition for reversibility will be met in a system of the kind considered if we have the equation

$$\frac{d}{dt}(\phi_0 \ \delta V_0) = 0 \tag{10}$$

holding at each point in the fluid, where ϕ_0 is the proper density of entropy as measured by a local observer at rest with respect to the fluid, and δV_0 is the proper volume of a small element of the fluid.

Since the proper volume in accordance with the principles of general relativity is dependent on the gravitational potentials $g_{\mu\nu}$, this condition for reversibility permits a mutual change in entropy density and gravitational field which was not contemplated in the classical thermodynamics. The equation states that the total entropy for each small element of fluid shall be constant as measured by a local observer, and this can evidently be met if the change in proper volume for the element occurs without flow of heat into the element, with exact balance between the internal and external pressures acting at the boundary of the element, and without irreversible processes taking place inside the element. In the case of the systems we are discussing the condition for no flow of heat into the element is evidently met in general on account of Eq. (6), and the exact balance between internal and external pressures is assured by the uniformity of pressure throughout the whole model as shown by Eq. (2); so that the avoidance of irreversible changes within the element is the only part of the requirement that must be specifically watched. If the requirement for reversibility is met, it will be noted that the changes taking place in the properties of the fluid filling our model of the universe would be those which would result from a reversible adiabatic change in volume of that kind of fluid.

[12] See reference 4, Eq. (18).

§ 6. Impossibility of a Strictly Periodic Solution

It can now be shown that the two separate sets of requirements for a strictly periodic solution could not both be satisfied by any fluid for filling the model of the universe which has reasonable physical properties.

On the one hand in accordance with the general expressions for density and pressure given by (2) and (3), and the necessary analytical requirement for a strictly periodic solution given by (9), we can evidently write

$$8\pi(\rho_1 - \rho_2) = \frac{3}{R^2}(e^{-g_1} - e^{-g_2}) \tag{11}$$

$$8\pi(p_1 - p_2) = -\frac{1}{R^2}(e^{-g_1} - e^{-g_2}) - (\ddot{g}_1 - \ddot{g}_2) \tag{12}$$

$$g_1 < g_2 \quad (13a) \qquad \text{and} \quad \ddot{g}_1 \geqq \ddot{g}_2 \tag{13b}$$

where $(\rho_1 - \rho_2)$ is the difference in energy density when the universe has its minimum and maximum volumes, and $(p_1 - p_2)$ is the difference in pressure.

On the other hand in accordance with the thermodynamic requirement for a periodic solution given in § 5, the changes in density and pressure when the universe passes from its minimum to its maximum volume must be those which would result from a reversible adiabatic expansion of the fluid, which would evidently give us

$$\rho_1 > \rho_2 \quad (14a) \qquad \text{and} \quad p_1 \geqq p_2 \tag{14b}$$

for any kind of fluid with which we might wish to regard the universe as filled.

All of the above relations, however, cannot be simultaneously satisfied. If the density is to decrease on expansion, then in accordance with (11) and (13a), it is evident that R must be real and R^2 positive. And with R^2 positive it will then be seen from (12), (13a) and (13b) that the pressure would increase on expansion, in contradiction to (14b).

It is evident that the relations (14a) and (14b) on which this reasoning is based would hold for any combination of incoherent matter and radiation which we might take as the fluid for filling the universe. By a special assignment of assumed properties, it might of course be possible to obtain strictly periodic solutions, but it does not appear probable that they would have actual physical interest. Thus a fluid which would correspond to the assumption made by Takéuchi,[13]

$$g = \sin kt \tag{15}$$

would appear to have very arbitrary properties.

§ 7. Analytical Requirements for a Quasi-Periodic Solution

In view of the above result we may now turn our attention to the possibility of quasi-periodic solutions, in which the proper volume of the universe increases from zero to an upper limit and returns, the mathematical analysis, however, failing to carry us through the exceptional point of zero volume. A

[13] See reference 8.

wide variety of possibilities presents itself for such solutions, and we may confine our attention for the present to those in which we take the constant R as real, and the cosmological constant Λ equal to zero as in Einstein's original simple form of the equations of relativistic mechanics.[14]

We can then obtain an expansion from zero proper volume $g_1 = -\infty$ to an upper limit $g_2 > g_1$ and return again to $g_3 = -\infty$, with reasonable values for density and pressure, if we place the following restrictions on g and its derivatives,

$$g_1 = -\infty \qquad \dot{g}_1 > 0 \qquad \ddot{g}_1 = -\infty \tag{16}$$

$$g_2 > g_1 \qquad \dot{g}_2 = 0 \qquad \ddot{g}_2 \leqq -\frac{1}{R^2} e^{-g} \tag{17}$$

$$g_3 = -\infty \qquad \dot{g}_3 < 0 \qquad \ddot{g}_3 = -\infty \tag{18}$$

In accordance with these restrictions, the model will evidently pass through a maximum volume at $g = g_2$. Furthermore, making use of the general expressions for proper density and pressure given by (2) and (3), the model will exhibit at the limits of the expansion, with $\Lambda = 0$, the densities

$$8\pi\rho_1 = \infty \qquad \text{and} \quad 8\pi\rho_2 \geqq 0 \tag{19}$$

and the pressures

$$8\pi p_1 = -\infty + \infty \quad \text{and} \quad 8\pi p_2 \geqq 0 \tag{20}$$

and these expressions evidently place no undue restrictions on the physical properties of the fluid with which we fill the model.

It is evident that solutions which agree with the conditions imposed by (16), (17) and (18) could not be regarded analytically as strictly periodic, since the value of $\ddot{g}$ is necessarily minus infinity at the lower limit of zero volume in order to prevent the pressure from becoming negative, and this is incompatible with the analytical conditions for a minimum. Nevertheless, it is evident physically that contraction to zero volume could only be followed by another expansion, and in addition, as noted by Einstein[7] in a similar connection, the idealization on which our considerations have been based can be regarded as failing in the neighborhood of zero volume. Hence from a physical point of view it seems reasonable to consider that solutions of the kind which we are considering could correspond to a series of successive expansions and contractions.

[14] The introduction of the cosmological term $\Lambda g_{\mu\nu}$ into the field equations of relativity was necessary for Einstein's static model of the universe. The term is not inevitably necessary, however, for nonstatic models, and Einstein (reference 7) now welcomes the opportunity to set it equal to zero. There are several arguments in favor of giving Λ the definite value zero. The equations of the theory are thereby simplified; the conclusions drawn from them are rendered less indeterminate; and it no longer becomes necessary to inquire into the significance and magnitude of what would otherwise be a new constant of nature. On the other hand, since the introduction of the Λ-term provides the most general possible expression of the second order which could be used for the energy momentum tensor, a definite assignment of the value $\Lambda = 0$ must be regarded as somewhat arbitrary and not necessarily correct.

§ 8. Thermodynamic Requirements for a Series of Identical Expansions and Contractions

Since the foregoing indicates the possibility of a series of expansions and contractions, we may next inquire into the further possibility that the successive expansions and contractions could have the character of identical repetitions. For this to be possible, it is evident that each expansion and contraction would have to be reversible from the point of view of relativistic thermodynamics, since any increase in entropy would prevent the return to an earlier condition.

If, however, the condition for thermodynamic reversibility

$$\frac{d}{dt}(\phi_0 \delta V_0) = 0 \tag{21}$$

already discussed in § 5 should be satisfied, a series of identical expansions and contractions would seem possible.

We may now discuss some quasi-periodic solutions fulfilling these requirements.

§ 9. Einstein's Quasi-Periodic Solution

As already mentioned one quasi-periodic model has already been suggested by Einstein. For simplicity denoting the "radius" of the universe by P where

$$P = Re^{g/2} \tag{22}$$

the general behaviour of the Einstein model can be most readily appreciated by solving the differential equation for P which he gives. We obtain

$$\sqrt{\frac{P}{P_0}} = \sin\left(\frac{t}{P_0} + \sqrt{\frac{P}{P_0}}\sqrt{1 - \frac{P}{P_0}}\right) \tag{23}$$

where P_0 is a constant, and note that the radius of the universe would expand from the value zero at $t=0$, to the upper limit $P=P_0$ at $t=\pi P_0/2$, and then return once more to zero at $t=\pi P_0$, the solution failing, however, to make P an analytical minimum at the lower limit.

The values of $\dot{g}$ and $\ddot{g}$ which correspond to (22) and (23) can be written in the form

$$\frac{\dot{g}^2}{4} = \frac{P_0}{P^3} - \frac{1}{P^2} \tag{24}$$

and

$$\ddot{g} = -3\frac{P_0}{P^3} + \frac{2}{P^2} \tag{25}$$

and substituting in the general expressions for pressure and density given by (2) and (3), with $\Lambda=0$ we obtain,

$$8\pi p_0 = 0 \tag{26}$$

$$8\pi\rho_{00} = \frac{3P_0}{P^3} = \frac{3P_0}{R^3 e^{3g/2}}\,. \tag{27}$$

The model thus corresponds to a universe filled with incoherent particles of matter, exerting no pressure, and unaccompanied by radiation.

From the point of view of the present paper, our interest lies in the entropy of the model. In accordance with the expressions for proper volume and density given by (4) and (27), it is evident that we shall have in the case of this model

$$\frac{d}{dt}(\rho_{00}\,\delta V_0) = 0 \tag{28}$$

owing to the fact that the only quantity g, which depends on the time, cancels from the product. For particles of matter exerting no pressure, it is evident, however, that the proper entropy $\phi_0\,\delta V_0$ will be proportional to the proper mass $\rho_{00}\,\delta V_0$ so that we must also have

$$\frac{d}{dt}(\phi_0\,\delta V_0) = 0 \tag{29}$$

which is the thermodynamic condition for reversibility already discussed in § 5. We may hence conclude that the model expands and contracts reversibly, which is perhaps an obvious conclusion in the case of this simple system. Since the behaviour of the model is thermodynamically reversible, there would be no thermodynamic hindrance which would prevent a continuous sequence of identical expansions and contractions.

§ 10. Quasi-Periodic Solution for a Universe Filled with Radiation

The real universe undoubtedly contains radiation as well as matter. The actual amount of this radiation is unknown. Nevertheless, it may be noted that as low a temperature as 12° absolute would correspond to a density of radiation of 1.7×10^{-31} gm/cm^3 which is approximately the same as Hubble's estimate[15] of the averaged-out density of visible matter in the universe. In any case it will be interesting to consider the extreme example of a model containing nothing but black-body radiation, even if we regard this merely as an intellectual exercise.

As mentioned above[16] I have already considered this model, without making any assumptions as to the value of the cosmological constant Λ, and come to the conclusion that no strictly periodic solution of the equations of motion could be found. The possibility of quasi-periodic solutions presents itself nevertheless, and setting $\Lambda = 0$, it can readily be shown that the line element for such a model then has the form

$$ds^2 = -\frac{At - t^2/R^2}{[1 + r^2/4R^2]^2}(dr^2 + r^2d\theta^2 + r^2\sin^2\theta d\phi^2) + dt^2 \tag{30}$$

where A is a positive constant.

[15] Hubble, Astrophys. J. **64**, 369 (1926).

[16] See reference 4.

In accordance with this form of the line element, the universe would start from zero proper volume at $t=0$, expand to a maximum at $t=AR^2/2$ and contract to zero again at $t=AR^2$, and the behaviour would be symmetrical on the two sides of the maximum as can easily be seen by transforming so that the zero of time comes at that point. Outside the range $t=0$ to $t=AR^2$, the treatment fails since the analytical expression would then correspond to negative volumes which are physically impossible.

The values of g and its differential coefficients corresponding to this line element are

$$e^g = At - t^2/R^2 \tag{31}$$

$$\dot{g} = \frac{1}{t} - \frac{1}{AR^2 - t} \tag{32}$$

and

$$\ddot{g} = -\frac{1}{t^2} - \frac{1}{(AR^2 - t)^2}. \tag{33}$$

Substituting these values into the general expressions for proper pressure and density given by (2) and (3), with Λ set equal to zero, we obtain

$$8\pi p_0 = \frac{1}{4}\,\frac{A^2}{(At - t^2/R^2)^2} \tag{34}$$

and

$$8\pi \rho_{00} = \frac{3}{4}\,\frac{A^2}{(At - t^2/R^2)^2} \tag{35}$$

We note at once that the energy density is always three times the pressure, so that the line element does correspond to a universe filled solely with black-body radiation, It is also interesting to observe that the energy density would be infinite at the times $t=0$ and $t=AR^2$ when the volume of the model is zero, and would drop to $3/R^2$ at $t=AR^2/2$ when the volume is at its maximum.

As in the case of the preceding model, our main interest for the present lies in the entropy of the system. In accordance with the known properties of black-body radiation, it is evident that we may write

$$\rho_{00} = aT_0^4 \quad \text{and} \quad \phi_0 = \frac{4}{3}\,aT_0^3 \tag{36}$$

for the proper (macroscopic) energy density ρ_{00} and proper entropy density ϕ_0 in terms of the Stefan-Boltzmann constant a and the proper temperature T_0. And by combination we can write

$$\phi_0 = \frac{4}{3}\,a^{1/4}\rho_{00}^{3/4}. \tag{37}$$

Substituting the values given by (35) and (31) we can then obtain for the entropy density

$$\phi_0 = \left(\frac{4}{3}\,a\right)^{1/4}\left(\frac{A^2}{8\pi}\right)^{3/4} e^{-3g/2} \tag{38}$$

and comparing with the general expression for proper volume given by Eq. (4), we at once see that we shall have the relation

$$\frac{d}{dt}(\phi_0 \delta V_0) = 0 \tag{39}$$

owing to the fact that the only quantity g, which depends on the time cancels from the product. This, however, is the condition for thermodynamic reversibility already discussed in § 5. Hence we may also conclude in the case of this model that there would be no thermodynamic hindrance which would prevent a continuous sequence of identical expansions and contractions.

§ 11. Quasi-Periodic Solution for a Universe Containing an Equilibrium Mixture of Matter and Radiation

It will also be interesting to consider the possibility for a quasi-periodic solution in the case of the model, which I have previously treated, of a universe containing a perfect monatomic gas in equilibrium with black-body radiation. If we set the cosmological constant Λ equal to zero, the equations of motion previously obtained[17] for this model become

$$8\pi p_0 = -\frac{1}{R^2}e^{-g} - \ddot{g} - \tfrac{3}{4}\dot{g}^2 = 8\pi(N_0 k T_0 + \tfrac{1}{3}aT_0^4) \tag{40}$$

$$8\pi\rho_{00} = \frac{3}{R^2}e^{-g} + \tfrac{3}{4}\dot{g}^2 = 8\pi(N_0 mc^2 + \tfrac{3}{2}N_0 k T_0 + aT_0^4) \tag{41}$$

$$N_0 = bT_0^{3/2}e^{-mc^2/kT_0} \tag{42}$$

where N_0 is the proper concentration of the gas in number of molecules per unit volume, T_0 the proper temperature, m the mass of one atom, and the constants k, a, c and b have their customary significance.

As demonstrated in the previous article these differential equations show no possibility for a strictly periodic solution of physical significance. To investigate the possibility for a quasi-periodic behaviour of the model, we shall not try to integrate the equations owing to their great complexity, but instead shall content ourselves with a demonstration of the existence of quasi-periodic solutions without obtaining their explicit form.

In accordance with Eq. (40) it is evident that the pressure p_0 is necessarily a positive quantity

$$p_0 \geqq 0 \tag{43}$$

since the concentration N_0 and temperature T_0 are both quantities which physically cannot be negative. Hence from (40), taking R as real, it is evident that we must also have

$$\ddot{g} \leqq -\frac{1}{R^2}e^{-g} \tag{44}$$

So that $\ddot{g}$ will always be negative if the volume of the universe is finite (i.e. $g < \infty$).

[17] See reference 5.

It appears evident, however, that this provides the possibility of choosing conditions so that models of the kind under discussion would pass through a point of maximum expansion. To prove this it is only necessary to admit the possibility of setting up a model of the universe with an equilibrium mixture of the gas and radiation contained in a finite volume which at the moment is not changing with the time. This set-up, with $\dot{g}$ put equal to zero and $\ddot{g}$ as seen above necessarily negative, evidently corresponds to the condition at the maximum point of expansion of a model which starts at zero volume with $\ddot{g}$ equal to $-\infty$ passes through a maximum with $\ddot{g}$ still negative and returns again to zero volume with $\ddot{g}$ again equal to $-\infty$. So that the conceivability of the proposed set-up shows the possibility of quasi-periodic solutions for models of the universe containing an equilibrium mixture of perfect monatomic gas and black body radiation.

It is also interesting to note that this method of showing the possibility for quasi-periodic solutions would apply to any model in which the fluid must be regarded as always exerting a positive pressure.

Since my previous work on this model showed that its expansion or contraction would be thermodynamically reversible, provided we make the somewhat arbitrary assumption that the matter in the model always immediately adjusts itself so as to remain in equilibrium with the radiation, it is evident in this case too that there would be no thermodynamic hindrance to a continuous succession of identical expansions and contractions.

§ 12. Conclusion

The result of the foregoing investigation of the theoretical requirements for the periodic behaviour of a certain class of nonstatic models of the universe has been threefold. In the first place, it has been shown that we cannot expect a strictly periodic solution of the equations of motion for such models, which would correspond to an oscillation in proper volume between a minimum and maximum value, unless indeed we should assign properties to the material filling the universe of a kind which would presumably not be of actual interest. It has been shown in the second place, however, that we might expect a wide variety of quasi-periodic solutions, which would correspond to an expansion of the model from zero proper volme to a maximum and return, —the solutions failing, however, to provide the analytical conditions for a minimum at the lower limit, even though physically contraction to this limit could only be followed by renewed expansion. Finally, it has been shown in accordance with the principles of relativistic thermodynamics that the conditions necessary for such quasi-periodic solutions could be met by systems which expand and contract reversibly without increase in entropy, so that there would be no thermodynamic hindrance to a continued series of identical expansions and contractions, and this conclusion has been illustrated by three examples.

The three models, which were chosen as examples to illustrate the possibility of a continued series of identical expansions and contractions, were,— first, a universe filled with incoherent matter exerting no pressure and unac-

companied by radiation,—second, a universe filled solely with black-body radiation,—and third, a universe filled with a mixture of perfect monatomic gas in equilibrium with black-body radiation. It is of interest, in connection with speculations as to the possibility that the actual universe might undergo a series of identical expansions and contractions, to find that so wide a range of models show such behaviour. This interest is increased, moreover, by the fact that my previous studies[18] of the second and third of these two models have shown that an ordinary observer would find a number of phenomena during the expansion of these models, such as the flow of radiation out into space and the annihilation of matter, which he would interpret as necessarily irreversible, in spite of the fact that all the processes taking place in such universes would really be reversible when analyzed from the legitimate point of view of relativistic thermodynamics.

In conclusion, however, we must not fail to emphasize that all our specific considerations have dealt with highly idealized models and not with the actual universe. These models have, moreover, some quite unsatisfying properties. In the first place, the models are all limited to a restricted class in which the properties of the contents of the universe, looked at from a large-scale point of view, are assumed to be the same throughout the whole universe at a given instant, and in justification of this assumption we merely have the data obtained from astronomical observations on the nebulae out to a limit of only about 10^8 light years. In the second place, moreover, the models do not concern themselves with many questions which may be very important for a satisfactory cosmological picture, such as the tendency of matter to conglomerate in stars and stellar systems,[19] the relative abundance of the different elements,[20] the relative concentration of matter and radiation,[21] and the rate at which matter and radiation adjust themselves to mutual equilibrium.[22] For these reasons we must not overestimate any insight that we obtain into the possible behaviour of the actual universe as a result of calculations on highly idealized models. Nevertheless, the principles of relativistic thermodynamics seem to have made a real contribution to cosmology, in showing that reversible models can at least be conceived which could exhibit a succession of identical expansions and contractions taking place at a finite rate.

[18] See references 4 and 5.

[19] The treatments which I have given to the flow of radiation in a universe, which is expanding reversibly, show that an ordinary observer in such a model would find a general outward flow of radiation from his region, but do not concern themselves with the more special problem of a directed outward flow from individual stars.

[20] I have shown, Jour. Am. Chem. Soc. **44,** 1902 (1922), that the relative abundance of hydrogen and helium appears to be very different from that demanded by thermodynamic equilibrium and similar findings have been obtained for the relative abundance of isotopes by Urey and Bradley, Phys. Rev. **38,** 718 (1931).

[21] The constant b in Eq. (42) would have to be enormous to secure appreciable concentrations of matter.

[22] The model of a universe containing an equilibrium mixture of gas and radiation would behave reversibly only if the mutual equilibrium were maintained. See reference 5.

PERMANENT ELECTRIC AND MAGNETIC MOMENTS OF CRYSTALS

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Abstract

In the first part of this paper the conditions for the existence of self-perpetuating electric moments in crystals are discussed. If these conditions are satisfied, the crystals must either show macroscopic electric moments or they will necessarily possess a definite type of a secondary structure. Certain complications may come in, however, if one is dealing with metals. Finally, the analogous magnetic case is qualitatively discussed.

§1. Introduction

THE theory of the ideal crystal lattices must be regarded as a complete failure as far as the treatment of structure sensitive properties is concerned. I have recently endeavored to show that a satisfactory theory of the physics of solids can be developed by introducing a secondary structure of crystal lattices.[1] This structure in general may be described as a periodic, very slight variation in density. I arrived at the conception of a secondary structure from purely theoretical arguments which threw doubt on the current conception of ideal crystals being thermally stable. Although many important conclusions of this theory were verified experimentally, its foundations are not very satisfactory for the following reasons.

In the first place, the procedure which I followed did not supply any unambiguous way of determining the exact nature of the deviations which transform an ideal lattice into a real and thermally stable crystal.

In the second place, it was very difficult to account for dimensions of the secondary lattice larger than a few hundred Angstroms, such as we have been finding in single crystals of metals. Although the theory does not really enable one to derive accurate values for the lattice constant D of the secondary structure there are strong reasons for assuming that approximately

$$D = d/(1 - d_P/d) \tag{1}$$

Here d is the ordinary lattice constant and d_p the corresponding spacing of a single plane of atoms which in itself is assumed to be in equilibrium under its own forces. The relative change from d to d_p can be estimated to be of the order of one percent, which according to (1) makes values of D larger than $100d$ very improbable. It also has been objected that it would be very hard to understand how actions over such large distances come about.

In the third place, experimental investigations carried out on single crystals suggest that there are secondary lattices of very different types. The theory therefore is confronted with the task of finding as many effects as

[1] F. Zwicky, Proc. Nat. Acad. Sci. **15**, 816 (1929); Helvetica Physica Acta **3**, 269 (1930); and **4**, 49 (1931).

possible which will render an ideal crystal thermally unstable. In addition, one has to try to find, if possible, a common denominator for all these effects. In a recent publication[2] I have advanced a tentative solution of this latter problem. The essence of my proposal was that those effects which are mainly responsible for the formation of a crystal at the same time necessitate a secondary structure. Those effects were recognized to be simultaneous cooperative actions between many particles. It seems therefore desirable to investigate more closely the characteristics of such actions. In this paper one very special phenomenon which depends on the cooperation of many particles will be considered. Its character will be best understood by studying some of its essential features in relation to a simple lattice.

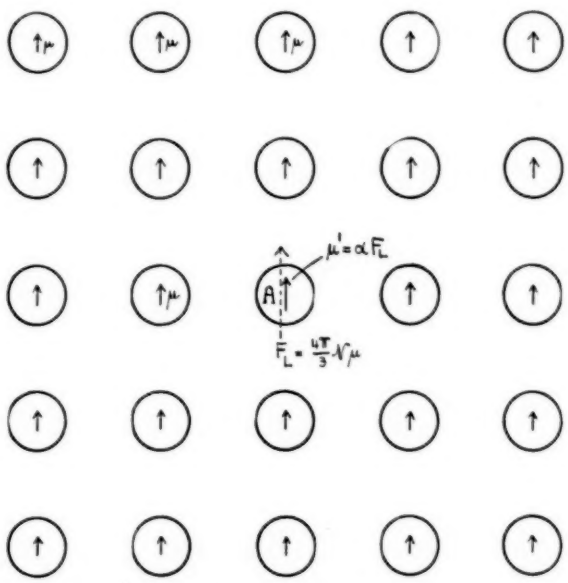

Fig. 1. Lattice of self-perpetuating dipoles.

§2. General Remarks on Self-Perpetuating Electric Moments

The essential part of this paper is devoted to a generalization of K. F. Herzfeld's considerations concerning the characteristics of metals. Herzfeld derives a criterion which decides whether or not an element will occur as a metal. His argument is roughly as follows:[3]

Consider a simple cubic lattice occupied by atoms whose dielectric constant is α. (See Fig. 1.) Suppose that all the atoms except A are endowed with an infinitely small electric dipole μ. Then because of the action of the μ's there will be an electric field at A which is equal to $F_L = 4\pi P/3 = 4\pi N\mu/3$, where N is the number of atoms per unit volume and P the polarization per unit volume.[4] The average field throughout the crystal of course is zero,

[2] F. Zwicky, Proc. Nat. Acad. Sci. September, 1931.
[3] H. F. Herzfeld, Phys. Rev. **29**, 701 (1926).
[4] See for instance P. Debye in Handbuch d. Radiologie, Vol. VI, p. 600.

provided that the lattice is infinitely extended. The so-called Lorentz field deforms the atom A and endows it with a moment μ'

$$\mu' = 4\pi N\mu\alpha/3. \tag{2}$$

Suppose now that

$$4\pi N\alpha/3 = 4\pi N\alpha\rho/3M = R\rho/M > 1 \tag{3}$$

where R is the molar refractivity, ρ the density, M the molecular weight, and $N = 6.06 \times 10^{23}$. It then follows that

$$\mu' > \mu.$$

This means that the assembly of the induced dipoles is a self perpetuating configuration of ever increasing moment. The process stops, of course, as soon as all the atoms are stripped of their loosest electrons. Condition (3) therefore is a condition for the element to be a metal.

It is very important to notice that the conclusions drawn above are valid only if α either increases or at least stays constant with increasing μ. This is probably generally true if α is the polarizability of an atom. We may, however, generalize Herzfeld's theory to systems with elementary units other than atoms, as will be shown in the next section. It then happens that the respective dielectric constant decreases with increasing polarization. The system involved may then jump into a configuration of permanent electric polarization without this process resulting in a collapse of the elementary particles, such as the stripping of atoms of their electrons. The permanent electric polarization need not be apparent in macroscopic dimensions, as will be shown later. In the case of a resulting macroscopic moment we are dealing with a crystal which possesses the characteristics of an electret. If only microscopic regions are electrically polar, they may compensate each other over large distances. We then obtain a peculiar type of a secondary structure.

In the next section we shall discuss the properties of a definite simple lattice which, however, is chosen so as to exhibit all the general features in which we are interested in our discussion.

§3. Permanent Electric Polarization in Cubic Face Centered Ionic Lattices

We investigate the properties of a lattice which is built up of positive and negative ions. We assume that for the mutual potential energy of two ions i and k we may write, as usually adopted for a first approximation,

$$\epsilon_{ik} = e_i e_k/r_{ik} + A/r_{ik}^p \tag{4}$$

where A and p for simplicity are taken to be the same for all the three possible combinations of the two ions.

The average energy ϵ of an ion in the face centered cubic lattice can be shown to be

$$\epsilon = -1.747e^2/r + \gamma A/r^p \tag{5}$$

with r designating the usual lattice constant. Numerical values of γ for different p's are tabulated in Table I.

TABLE I.

p	5	6	7	8	9	10
γ	166	269	478	888	1700	3287

Now for this lattice to be in equilibrium we must require

$$\frac{\delta\epsilon}{\delta r} = 0 \text{ for } r = d \tag{6}$$

or

$$A = 1.747e^2d^{p-1}/p\gamma. \tag{6'}$$

It is usually assumed that this condition is all that is required in order to make a lattice of the described type dynamically stable. Indeed, in all the cases dealt with in the literature it was found that a lattice of the above type, with A equal to (6') is also stable against a linear extension, shearing, or against a displacement of the whole negative lattice relative to the positive lattice, etc. However, there was known no general proof that condition (6) insures the complete dynamic stability of the lattice. In fact, it can be shown that this is not at all the case. For this purpose we shall investigate more closely the stability of our model with regard to relative displacements of the negative and the positive lattice. Such displacements evidently may be caused by external electric fields. It is well known that the characteristic frequencies involved correspond to the frequencies of the residual rays.

Suppose that the lattice of the positive ions is given a uniform infinitesimal displacement ξ in the direction of the [100] axis. At the location of each ion a Lorentz field

$$F_L = 4\pi P/3 \tag{7}$$

is created, with (7') $P = Ne\xi/2$ and $N = 8/d^3$

$$F_L = 16\pi e\xi/3d^3. \tag{8}$$

The energy per molecule (negative and positive ion) is equal to

$$\Delta u^- = -e\xi F_L/2 = -8\pi e^2\xi^2/3d^3. \tag{9}$$

There is also a change of energy Δu^+ due to the forces of repulsion. Summing up the individual contributions of all the neighboring atoms one finds for Δu^+ per molecule

$$\Delta u^+ = 4p(p-1)\left[2^p + \frac{4}{9}\left(\frac{2}{3^{1/2}}\right)^p + \frac{4}{5}\left(\frac{2}{5^{1/2}}\right)^p + \frac{4}{9}\left(\frac{2}{3}\right)^p + \cdots\right]\frac{A}{d^{p+2}}\xi^2. \tag{10}$$

Values of the numerical factor (h) for different p's are tabulated in Table II.

TABLE II.

p	5	5	7	8	9	10
h	2680	7860	21800	57700	148000	369000

For the total change of energy per molecule we obtain, therefore,

$$\begin{aligned}\Delta u &= [-8.4e^2/d^3 + hA/d^{p+2}]\xi^2 \\ &= 1.75e^2/d^3 \times [-4.8 + h/p\gamma]\xi^2.\end{aligned} \tag{11}$$

The numerical values of $h/p\gamma$ are given in Table III.

TABLE III.

p	5	6	7	8	9	10
$h/p\gamma$	3.23	4.87	6.51	8.10	9.67	11.2

From this table we derive the remarkable conclusion that Δu for p slightly smaller than 6 becomes negative. This is a very remarkable result indeed. It means that a cubic crystal of the described kind will voluntarily jump into a state of permanent electric polarization. Unlike the analogous case of atoms, no destruction of the lattice will take place because of the fact that it becomes

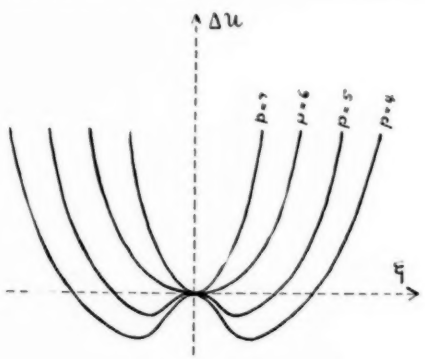

Fig. 2.

more and more difficult to move the two lattices apart as ξ increases. The self-perpetuating movement of the two lattices will therefore stop at some definite value ξ_e of ξ. Fig. 2 shows the energies Δu plotted schematically as a function of ξ for different values of p. The ideal crystal is dynamically stable with regard to a variation ξ only if $p>6$. For $p<6$ it is dynamically unstable. The equilibrium position in this case is given by the minimum of Δu. It corresponds to a state of permanent electric polarization.

The most important result of the above investigation is this. Suppose that we build up a model of a crystal lattice by assuming a certain potential energy function for the mutual interaction of the two particles in the lattice. This energy function may contain certain parameters, A and p in our case. If A and p are determined by adjusting certain characteristics of our model to certain given experimental data (lattice constant, compressibility), one cannot be assured that the model is dynamically stable. Indeed, the particular model discussed above is stable against a uniform pressure because of A having been properly adjusted by (6′). The model also turns out to be stable if a linear extension or a shear is considered. However, for $p<6$ it is unstable against a relative motion of the positive and negative partial lattices.

§4. Generalization of the Model Used in the Previous Section

It is obvious that the computations given in the previous section need to be generalized in various ways.

In the first place, our calculation involves implicitly the assumption that no change of dimensions normal to the relative displacement ξ of the two partial lattices is involved. This is certainly not correct, and additional terms must be introduced. For the present discussion it is sufficient to notice that this lateral effect can only increase the initial instability of the lattice.

In the second place, it will be necessary to compute Δu to higher order terms in ξ in order to determine the final equilibrium position ξ_e. It will, however, be of interest to do so only if one is sure that a certain model actually is a good approximation of the real crystal. More about this will be said in section 5.

In the third place, we must take into account that the ions themselves are deformable. The Lorentz field is as before $F_L = 4\pi P/3$. The expression (7′) for the total moment P per cm³ is changed to

$$P = N\mu/2 + N\mu_0 \tag{12}$$

with

$$\mu = e\xi \quad \mu_0 = \alpha F_L \tag{13}$$

if we use the same notation as in the previous section. Therefore

$$F_L = 4\pi N/3[e\xi/2 + \alpha F_L] \tag{14}$$

or

$$F_L = 2\pi N e\xi/(3 - 4\pi N\alpha). \tag{15}$$

It is evident from the order of magnitudes of $N \sim 10^{23}\text{cm}^{-3}$ and $\alpha \sim 10^{-24}\text{cm}^3$ that the denominator may be considerably smaller than 3, or F_L considerably larger than the corresponding expression with α equal to zero.

In order to get an idea about the magnitude of the Lorentz fields and the corresponding energies involved, we assume that our model has a lattice constant equal to that of rock salt, $d = 5.6 \times 10^{-8}$ cm. For $\xi_e = 10^{-10}$cm we obtain $F_L = 1.36 \times 10^6$volts. The energy per molecule due to this field is

$$\Delta u^- = \Delta u_1^- + \Delta u_2^- = -e\xi/2 - \alpha F_L^2/2 \tag{16}$$

or in our case $\Delta u_1^- = -1.06 \times 10^{-16}$ergs. The energy Δu^- is proportional to ξ^2. It therefore can easily assume values equal to kT say near to the melting point, with ξ amounting to only a few percent of the lattice constant. This is very important because of the fact that certain phenomena may be observed calorimetrically without being easily detectable by a structure investigation with x-rays.

§5. On a New Type of a Secondary Structure

We are now coming back to some of the ideas which have already been mentioned in the introduction.

Suppose that we are dealing with an ionic cubic face centered lattice whose equilibrium configuration is characterized by a permanent electric polarization, due to a value $p < 6$ in relation (4). It is obvious that there are

forces operative during the growth of the crystal which tend to prevent its building up an electric moment. These forces originate on the necessarily existing surfaces. If, for instance, the crystal grows as a large plate a depolarizing field equal to $4\pi P$ will be set up by the surfaces if P is directed normal to the plate. This because of the bound surface charges originated by the electric polarization itself. If the external shape is a sphere or a cube the depolarizing field will be $4\pi P/3$, which still is sufficient to compensate for the Lorentz field. The neutralizing action of the surfaces can be disregarded only if the crystal grows in form of a long needle or if there are charges present which compensate for the action of the surfaces by covering them with charged layers. The bound and the real charges on a surface in this case form double layers with no corresponding external fields. It seems very artificial and unsatisfactory to introduce accidental conditions of this kind. If possible the crystal will favor some kind of an arrangement which allows it to assume

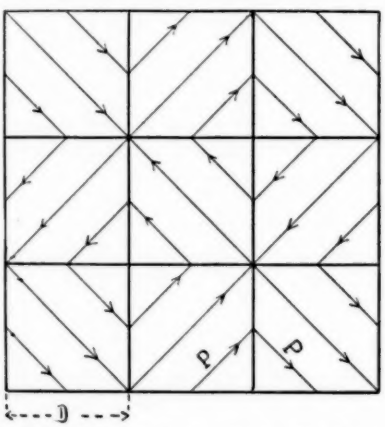

Fig. 3. Permanent electric polarization in crystals.

the configuration of lowest energy without making use of any special external condition. Arrangements of this kind probably must possess the same symmetry character as the primary structure. Fig. 3 gives an illustration of a possible arrangement. It is based on the idea of avoiding neutralizing surfaces by arranging the Lorentz field vectors in circles or in squares conforming with the cubic character of the primary structure as nearly as possible.

In a three-dimensional lattice the secondary structure resulting from a self-perpetuating polarization may be derived by the following simple method, which has been suggested to me by Dr. H. M. Evjen. First think of the crystal being subdivided into identical square needles which are parallel to the [100] direction. Polarize these needles alternately in the [100] and [100] directions. This process is now repeated for the [010] and the [001] direction in such a way that each intersection of three needles is a cube. The resulting vectors representing the polarization evidently will lie in one of the four space diagonals of the cube.

From Fig. 3 it is evident that the crystal will exhibit a certain peculiar type of secondary structure. In the thermodynamically stable state this

structure may be expected to be an absolutely regular one characterized by a greater lattice constant D. An approximate relation between D and the usual smaller lattice constant d may be derived as follows:

The permanent electric polarization causes a relative change Δ in dimension lateral to it. We consider two adjacent regions whose vectors P are at right angles to each other. These two regions can be approximately in phase with each other only over a distance smaller than $D = d/\Delta$. In fact, if a positive and negative ion face each other at A, then at a distance $D/2$ away from A, two ions of the same sign are in opposition, provided that the dividing line between the two parts of the crystal is of the type [100]. We therefore have to keep our regions in Fig. 3 smaller than D or we will begin to loose energy along their boundaries. This means that the new type of a secondary structure proposed in this section is characterized by a greater lattice constant approximately equal to

$$D = d/\Delta. \tag{17}$$

We have seen in section 4 that values of ξ_e equal to 10^{-9} cm lead to reasonable moments such as have been observed in certain crystals, Rochelle salt, for instance. The quantity Δ will of course depend on ξ_e and therefore have a very wide spread. In general Δ will be very small. Therefore

$$D \gg d.$$

This is a very satisfactory result, inasmuch as it may provide an understanding of such remarkably large spacings of the order of 1μ as we have observed for the secondary structure of certain metals. It is a very interesting problem to find out whether the observed secondary structure of metal single crystals can be traced back to the origin proposed here. Although I cannot offer a complete solution of this problem, I should like to advance some tentative suggestions which might prove valuable.

According to the theory of Herzfeld which I have sketched in section 2, electrons are stripped from sufficiently dielectric atoms embedded in solid matter. If the polarizability is increasing with increasing moment, we must conclude that the electrons try to get away from the remaining ions as far as possible. This behaviour, which seems very strange at first sight, is due to the existence of a self perpetuating polarization. We therefore arrive at the following picture of a metal with say one stripped or free electron per atom. We suppose these atoms to be arranged in a face centered cubic lattice. The electrons will exhibit a tendency to arrange themselves in a similar lattice which, however, is displaced by half the lattice constant in one of the principal directions say [100]. Electrons and ions are thus in the same relative position to each other as the ions in NaCl. This is the picture of a simple metal which F. Haber has advanced many years ago. Of course one must not think of such an arrangement as a static one. If it were static the lattice formed by the electrons could be detected with x-rays, which is not the case. The problem to be solved is to find the interaction between the electron lattice or electron gas and the remaining ions. From the fact that a static arrangement

of charges is unstable (law of Earnshaw), it seems probable that the interaction between the two lattices is such that a simplified expression for the mutual energy of an electron and an ion would require an exponent $p<6$. This suggests that metals form crystals whose equilibrium configurations are characterized by permanent electric moments. The formation of macroscopic moments would again be prevented by the building up of a secondary structure. From this viewpoint the large lattice constants $D=5000$–20000A which we have observed in different metals appear comprehensible.

Finally, a few words about the alkali-halides. For most of them $p>6$. Therefore they do not fall within the range of our present considerations, unless a combination of a relatively small p together with a large polarizability α makes them eligible for a secondary structure of the type described above. This may be the case, for instance, for PbS. According to (15) F_L must be multiplied by a factor

$$f = 3/(3 - 2\pi/\Gamma)$$

if α is not neglected. Here $\Gamma = a^3/2\alpha$ and $a = d/2$. Now for PbS we have $\Gamma = 2.54$ and therefore $f \sim 6$. This would put PbS into the category of crystals with permanent moments in microscopic regions, for almost any value of p, which may be the explanation of why PbS and PbTe behave so differently from the other alkali-halides.

§6. Permanent Magnetic Moments of Crystals

A ferromagnetic crystal may in some respects be regarded as the magnetic analogue to a crystal possessing a permanent electric moment. However, there are some conspicuous differences between the two cases. In the electric case the back coupling of the induced dipoles in established by the Lorentz field $F_L = 4\pi P/3$. To account for the ferromagnetism in Fe, Ni, Co, etc. according to P. Weiss back-coupling fields of the order 10000 M must be introduced, where M is the magnetic polarization per unit volume. In spite of this enormous back-coupling factor, namely 10000 instead of $4\pi/3$, a single crystal of iron is not magnetic as a whole. This is a very puzzling fact. Indeed it is hard to understand why the crystal should not be uniformly magnetized, as the largest possible demagnetizing factor 4π falls far too short from compensating the enormous factor 10000. This problem has not found a satisfactory solution so far. Whatever this solution may be, it seems safe to conclude that it must involve the existence of a secondary structure of magnetic origin. For, although an iron crystal is not magnetized as a whole it must be magnetized in parts, because of the magnetization betraying itself in the caloric behavior of the crystal (rise of the specific heat below the Curie point, etc.). A magnetic secondary structure therefore exists. Off hand it is impossible to say whether the elementary regions are fibers or cubic blocks or of some other shape. However considerations analogous to those leading to Fig. 3 make it possible to determine the exact shape. Assuming them to be cubic, F. Bitter[5] has suggested various ways for estimating their size. He finds that they contain

[5] F. Bitter, Phys. Rev. **37**, 91 (1931).

approximately 350000 atoms each. If we wish to make a theoretical estimate we must apply some relation similar to the one used in the electric case (17)

$$D = d/\Delta$$

where Δ now stands for the relative change in length due to magnetostriction caused by the magnetic saturation. Unfortunately there is no way so far to obtain Δ. If Bitter's estimates are correct, then Δ must be of the order of 1 percent.

It is very interesting to notice that ferromagnetic crystals behave abnormally in regard to plastic deformation. Single crystals ordinarily glide along certain planes belonging to a discrete crystallographically determined set. In iron, however, only the [111] direction is distinguished, but any plane through it may be a slip plane.[6] This becomes comprehensible if one considers that the elementary parts of the magnetic secondary structure of iron are slightly tetragonal. Adjacent blocks are in phase only for distances less than 200A making use of Bitter's estimate. Iron is therefore, in a way, much more similar to an amorphous substance than to other metal crystals whose secondary structures are characterized by spacings of the order of 1μ. It is to be hoped that if iron single crystals are annealed and distorted in a magnetic field that they also will exhibit definite crystallographic slip planes. Experiments to check this are being carried out at this Institute.

§7. Concluding Remarks

I have recently proposed a scheme which was intended to provide a general working basis for the physics of crystals. I showed that those phenomena which essentially characterize the crystalline state are due to the simultaneous cooperation of many particles in regard to a line-up in space. There are different types of such cooperative effects. The main purpose of this paper is to point out two of them which are related to the formation of permanent electric and magnetic moments in crystals. I also attempted to show in which way these two effects may be the cause of a secondary structure of crystals.

[6] G. I. Taylor and C. F. Elam, Proc. Roy. Soc. **A112**, 337 (1926).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Magnetization of Colloidal Suspensions

If one assumes the Weiss-Heisenberg postulate of spontaneously magnetized "domains," then it is difficult to see how it is possible to demagnetize a ferromagnetic body. The recent work of Akulov,[1] Powell,[2] and Bitter[3] has done much to resolve this difficulty, but it would still be desirable to obtain more direct experimental evidence of the existence of these domains, as all investigators in this field are not yet fully convinced of their reality. An estimate of the size of these domains can be made from the rate of the approach to saturation of the material in high fields. Such a calculation has recently been made by Bitter,[3] with the result that a group containing approximately 10^5 atoms would constitute a domain. This corresponds to a linear dimension of the order of 150 mμ. Hence if we could divide a ferromagnetic body into particles this small, we should expect each particle to be magnetically saturated.

Colloidal suspensions of nickel or iron can be obtained with this order of particle size, and an investigation of their magnetic properties should be interesting. In suspensions of this character, the concentration of the particles would be so small that the effect of one particle on another could be neglected. The suspension would thus be equivalent to a gas composed of large molecules, and its magnetic moment would be given by the Langevin formula

$$N\mu = N\mu\left(\coth\frac{\mu H}{kT} - \frac{kT}{\mu H}\right)$$

where N is the number of particles per cc, and μ the magnetic moment of each particle. For a particle of nickel of diameter 150 mμ, we have a saturated magnetic moment of 7.0×10^{-12} c.g.s. m per particle, and if we take a field of 1000 gauss and $T=300°$K, then $\mu H/KT$ has the value 1.7×10^5. Under these conditions, the suspension as a whole will have a magnetization within 10^{-3} percent of that possible at this temperature. If, however, we decrease the magnetic moment of the particle by reducing its size, the Brownian rotations of the colloidal particles will become important, since the magnetic moment will assume directions determinate with respect to the directions of the crystal axes, and $\bar{\mu}$ will become smaller than μ. We might thus trace out a Langevin curve. The same result can, of course, be accomplished by varying either the field of the temperature, but the feasible range of variation of H or T, especially of the latter, is much less than that of μ.

Such evidence would, of course, constitute a very direct proof of spontaneous magnetization of small particles. A suspension of particles of this character would also show other interesting properties. It should exhibit a magnetic viscosity which would be directly dependent on the viscosity of the medium in which the particles are suspended, and there should be no hysteresis of the ordinary kind.

CAROL G. MONTGOMERY

Sloane Physics Laboratory,
Yale University,
October 3, 1931.

[1] Akulov, Zeits. f. Physik **69**, 78–99 (1931) and earlier papers.

[2] Powell, Proc. Roy. Soc. **A130**, 167–181 (1930).

[3] Bitter, Phys. Rev. (2) **38**, 528–548 (1931).

Equivalent Electrical Networks

In a recent article [Phys. Rev. **37**, 1583 (1931)] N. Howitt discusses a method of deriving networks equivalent to a given structure. This method depends on the preservation of the positive-definite (or semi-definite) character of three quadratic forms associated with the network, in an affine transformation of these forms. If this transformation be written $i_s=\sum_r c_{sr} i_r'$, then for equivalence with respect to driving point impedance in the jth mesh it is necessary only that all c_{sr} be real, $c_{jj}=1$ and $c_{jk}=0$ when $j\neq k$.

Certain subsidiary conditions leading to further restrictions on the coefficients are mentioned by Howitt, *viz* that "the self-parameter of every mesh be greater than its total mutual parameters with respect to other meshes." The latter condition is unnecessary if a generalized conception of mutual parameters be admitted. For inductances this is nothing more than the usual conception of mutual inductance; the property of being positive-definite is sufficient for a quadratic form to represent a physical system of self and mutual inductances. Such a system may, however, be replaced by an equivalent system of self-inductances and ideal transformers whence it is at once evident that positive-definite forms associated with resistances and capacitances can also be represented with the aid of ideal transformers. From the practical point of view such ideal transformers may be objectionable but from the theoretical standpoint we must accord them the same privileges as pure inductances, pure capacitances, or pure resistances. No other restrictions on the c_{sr} than those mentioned in the first paragraph are therefore necessary for physical realizability.

Howitt notes the possibility of extending the method of affine transformation to equivalence with respect to driving point impedance in more than one mesh. It should be observed, however, that equivalence with respect to driving point impedance in any two meshes necessarily entails equivalence with respect to the mutual impedance between these meshes. Conversely no equivalence with respect to mutual impedance can be obtained by this method without having equivalence with respect to the corresponding self-impedances.

While the method of affine transformation gives a large class of equivalent networks, it can be shown that it does not always lead to *all* equivalent networks. By use of Howitt's notation a network may be characterized by the matrix $\|a_{rs}\|$ where $a_{rs}=\lambda_{rs}p+\rho_{rs}+\sigma_{rs}p^{-1}$. The affine transformation which leaves invariant the driving point impedance $Z^{-1}(p)=\delta \log|\delta_{rs}|/\delta a_{ii}$ will also leave invariant the derivatives $\partial \log|\lambda_{rs}|/\partial\lambda_{ii}$, $\partial \log|\rho_{rs}|/\partial\rho_{ii}$, $\partial \log|\sigma_{rs}|/\partial\sigma_{ii}$. The latter are not necessarily invariant at the same time as $Z(p)$. In particular it can be shown that several values of $\partial \log|\rho_{rs}|/\partial\rho_{ii}$ are sometimes possible for networks with a given $Z(p)$, the number of possible values depending on the particular $Z(p)$ prescribed. Moreover, the number of meshes in such networks is not necessarily fixed (not counting the trivial case where additional meshes arise from proportional impedences in parallel). This point has been discussed at greater length in a paper by the present writer in a forthcoming issue of the Journal of Mathematics and Physics entitled: "Synthesis of a Finite Two-terminal Network whose Driving-point impedance is a Prescribed Function of frequency."

The problem of finding *all* equivalent networks has not yet been completely solved.

O. BRUNE

Massachusetts Institute of Technology,
Cambridge, Mass.,
September 28, 1931.

Reaction Due to Gas Molecules Leaving the Cathode of an Arc

Wellman[1] has suggested recently that the evolution of gas from the cathode of a vacuum arc may account for the large reaction upon the cathode observed by Tanberg.[2] As Mr. Tanberg is no longer in these Laboratories, the writers have examined Tanberg's original results for additional data, not contained in his paper, which may be of value in calculating the effect of the gas coming from the cathode.

Unfortunately, due to a typographical er-

[1] Wellman, Phys. Rev. **38**, 1077 (1931).
[2] Tanberg, Phys. Rev. **35**, 1080 (1930).

ror, the value of current in Table III of Tanberg's paper[2] appears as 2.3 amps. instead of 23 amps. as it should. The value for the force pressure rise from 5×10^{-3} to 100×10^{-3} mm For a series of tests, Mr. Tanberg recorded the following results:

Current	Arcing time	Pressure before test	Pressure after test
23 amps.	6.4 sec.	0.6×10^{-3} mm	15×10^{-3} mm
23	7.6	0.1×10^{-3}	55×10^{-3}
23	3.0	0.1×10^{-3}	20×10^{-3}
23	4.4	0.8×10^{-3}	20×10^{-3}
23	3.3	0.6×10^{-3}	11×10^{-3}

of the evolved gas calculated by Mr. Wellman, which for a current of 2.3 amps. came to the same magnitude as the measured force on the cathode, must therefore be reduced by a factor of 10.

Actually, in comparing the reaction of the escaping gas with the total force on the cathode, one should use the total weight of gas liberated, the arcing time, and the measured force for the same test. Such complete data for any one test are not available. The arcing time varied from 3 to 15 seconds, and the

The volume of the vessel used in the experiment was 5750 cm³; with the associated vacuum system, the total volume was approximately 7000 cm³. The pressure was read upon a McLeod gauge, within perhaps a minute after the arcing ceased.

R. C. Mason
W. E. Berkey

Research Laboratories,
W. E. & M. Co.,
East Pittsburgh, Pa.,
September 23, 1931.

The Structure of the Water Vapor Molecule

The fine structure of water vapor in the more intense bands has been studied recently by Plyler and Sleator.[1] The work on the band at 1.87μ has been repeated by the writer, using higher resolution. Also the region of 1.40μ has been studied and about 100 lines were observed in the harmonic of the strong band at 2.67μ. This band has the appearance of a double type band with much more absorption on the longer wave-length side. Or it may be a zero branch type much distorted. If of the double type, the center is at 1.3765μ, and if of zero type, the center is at 1.3842μ.

In the band at 1.87μ a region has been found which has the appearance of the 6.26μ band. The first three lines on each side of the center have about the same spacing and intensity variation as found in the 6.26μ band. Some of the other lines also correspond but not completely as two bands overlap somewhat in this region. This region appears more like a definite band when small amounts of water vapor are used. The center is at 1.8835μ. If this value is used as a fundamental frequency with that at 2.67μ and 6.26μ, we find the half angle $\alpha=57\ 30'$, or the total angle is 115° between the lines connecting the oxygen atom to the two hydrogen atoms. The calculated intensities for the three fundamentals check well with the observed intensities. Also all the smaller bands which have been observed for water vapor correspond to combination or overtones of these three bands.

It is interesting to note that this value of the angle for water vapor is of the order of magnitude as predicted by Slater[2] in his theory of directed valence.

E. K. Plyler

Physics Department,
University of North Carolina,
October 10, 1931.

[1] E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

[2] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

Diamagnetic Susceptibility of the Rare Gas Atoms According to Slater's Method

Diamagnetic susceptibility of a symmetrical atom is given by $\chi=-(-e^2)/(6mc^2)\Sigma\bar{r^2}$ where $\bar{r^2}$ is the mean square distance of an electron from the nucleus, Σ means that the summation extends over all the electrons in the atom. By evaluation of an approximate

TABLE I. *Susceptibilities and charge distributions of electron shells according to Slater.*

Electron groups	Kr $Z-S$	Kr $-\chi.10^6$	Xe $Z-S$	Xe $-\chi.10^6$	Nt $Z-S$	Nt $-\chi.10^6$
$2s, p$	31′855	0′19	51′85	0′07	81′85	0′03
$3s, p$	24′7	1′33	42′7	0′45	74′7	0′15
$3d$	14′8	4′61	32′8	0′95	65′5	0′26
$4s, p$	8′2	31′75	26′2	2′54	58′2	0′49
$4d$		37′88	14′8	9′89	46′8	0′99
$5s, p$			8′2	34′94	40′2	1′44
$4f$				48′84	27′4	4′05
$5d$,					14′8	13′17
$6s, p$					10′3	25′98
						46′56

wave function, Slater (Phys. Rev. **36**, 57, 1930) has given a method of calculating $\Sigma r^{\bar{2}}$ in terms of the effective principal quantum number n^* and of the effective nuclear charge $(Z-S)$ for any one electron in a group by an equation

$$\Sigma r^{\bar{2}} = [(n^*)^2(n^* + \tfrac{1}{2})(n^* + 1)]/(Z - S)^2$$

According to Slater, n^* is assigned values of 1, 2, 3, 3′7, 4′0, and 4′2 in place of $n = 1, 2, 3, 4, 5$, and 6, for the successive electron shells from K to P. $(Z-S)$ is evaluated for different groups of electrons $1s$; $2s, p$; $3s, p$; $3d$; $4s, p$; $4d$; $4f$, $5s, p$; $5d$; $6s, p$; etc.—in such a way that s and p electrons of a group are taken together but d and f are separated. Susceptibilities calculated by this method seem to be in better accord than by Pauling's or by Hartee's distribution of charge method. Hence it is proposed to give in Table I the susceptibilities and the charge distributions of the corresponding electron groups of the rare gas atoms Kr, Xe, and Nt for which experimental values are not known.

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Physics Department,
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Bengal, India,
October 3, 1931.

The Equation of State of Real Gases

The usual theoretical equations of state are derived by the use of phase integrals extended over the entire phase space of the system, i.e. the integrations performed are carried out over all possible velocities of all molecules. Such treatment is defective for the following reason: If there exists between all pairs of molecules a potential energy $\epsilon(r)$ which has a minimum, then there are discrete energy states, and all phase space is no longer accessible in the classical sense. For light gases the part of phase space thus excluded is appreciable and must be corrected for in the equation of state.

We obtain the pressure of a gas from the relation

$$p = kT(\partial/\partial V) \log Z, \qquad (1)$$

where Z is the complete partition function (Zustandssumme) of the gas. The gas will be considered as a mixture of n pairs of molecules in quantized collision states, whose interaction with similar pairs and with "free" molecules may be neglected. Z then consists of two factors, S^n, associated with the first mentioned pairs, and Z_p, belonging to the free molecules. S in turn is represented by

$$\Big(\sum_i e^{-E_i/kT}\Big)\Big[\frac{(2\pi mkT)^{3/2}V}{h^3}\Big] \qquad (2)$$

where the first factor, in which E_i denotes the discrete energies, results from the internal motions, the second being due to the classical motion.

Z_p is the ordinary phase integral for the gas, but the integrations are to be carried out only over the accessible domain: for all pairs of molecules in collision the velocities in the integrand of Z_p must be integrated from sets of values corresponding to a kinetic energy ϵ to $\pm\infty$. ϵ depends on the relative coordinates of the molecules, hence the result of the velocity integration appears as a variable in the volume integration.

As does the complete phase integral in the usual theory, Z_p decomposes into products of integrals over the phase space of pairs of molecules, if only binary collisions are considered. We obtain a result formally similar to

the ordinary one:

$$Z_p = \left(\frac{m^3}{h^3} gV\right)^N (1+z)^N. \tag{3}$$

Here $g=(2\pi kT/m)^{3/2}$, N is the number of "free" molecules, and

$$z = \frac{N}{2g^2V^2}\left\{\int_{\text{all ph. sp.}} Id\omega - \int_{\text{excluded ph. sp.}} Id\omega\right\} \tag{4}$$

The integrand I is

$$e^{-m/2kT(v_1^2+v_2^2)}(e^{-\epsilon(r_1-r_2)/kT}-1).$$

The first integral in (4) can be evaluated easily and gives the classical result $4\pi g^2V\int(e^{-\epsilon/kT}-1)\,r^2dr$, while the second can be expanded into a series which converges rapidly for most cases of physical interest:

$$4\pi g^2V\int\phi\left(\frac{-\epsilon}{kT}\right)(e^{-\epsilon/kT}-1)r^2dr.$$

$$\phi(x)\begin{cases} = 0.273x^{3/2} - 0.085x^{5/2} + 0.019x^{7/2} \\ \quad - 0.001x^{9/2} + \cdots, \\ = 0 \text{ for } x < 0. \end{cases}$$

Combining 1, 2, 3, 4 we notice that the first factor of S contributes nothing to p since it does not depend on V. The second, of course, produces the partial pressure nkT/V, which, because n is always very small compared with N, needs not be considered. Since $z \ll 1$, $\log(1+z)$ is simply z, and we are led to

$$p = \frac{NkT}{V}\left\{1 - \frac{2\pi N}{V}\int\left[1-\phi\left(\frac{-\epsilon}{kT}\right)\right](e^{-\epsilon/kT}-1)r^2dr\right\}. \tag{5}$$

The coefficient of $1/V$ in $\{\}$ is known as the second virial coefficient B. (Eq. (5) does not agree with an expression published in this column by Kirkwood and Keyes, August 1, which I have been unable to verify.)

A numerical application of (5) to gases like He or H_2 shows that the correction which is to be made on the classical B values even at low temperatures is not as large as has frequently been supposed. For helium in particular, all theoretical data for a calculation of B are now available, but it is only fair to say that, while things agree well at high temperatures, the result at low temperatures is quite embarrassing. If in the expression for ϵ only the part of the mutual energy arising from dipole forces is used, and in (5) only the classical part ($\phi=0$) is retained, as was done by Kirkwood and Keyes (Phys. Rev. **37**, 832, 1931) then the agreement at low temperatures of B with experimental data is fair. Moreover, if the correction given by (5) is applied, the agreement becomes very satisfactory indeed. However, the inclusion in ϵ of quadrupole forces, recently calculated (Margenau, Phys. Rev. **38**, 747, 1931), destroys the agreement completely. The best experimental value for B_{He} at 20°K is about -4. The theoretical value, computed classically, turns out to be about -24, and the use of (5) reduces it only to -21. This state of affairs offers a strong temptation to ignore the quadrupole forces completely and to look for reasons why they should be ineffective; but we find it impossible to entertain any doubt regarding the necessity of their inclusion. We are unable at present to offer an explanation of this discordance.

HENRY MARGENAU
Sloane Physics Laboratory,
Yale University,
October 12, 1931.

Auto-Ionization in the Noble Gases and Alkaline Earths

The recent explanation by Shenstone (Phys. Rev. **38**, 873, 1931) that the "*ultra-ionization potentials*" observed for mercury vapor are due to an "*auto-ionization*" process of the atom appears to be correct since it accounts very beautifully for certain well-known anomalies in the spectra of many elements. One of these anomalies, as pointed out by Shenstone and to be given later, is the well-known diffuseness of certain lines in the arc spectrum of Cu.

In the inert gases all observed series approach the inverted $^2P_{\frac{1}{2}, 1\frac{1}{2}}$ level of the corresponding ions. With almost perfect *jj*-coupling in krypton and xenon each series of energy levels arising from p^5ms, p^5mp, p^5md, and p^5mf, consists of two distinct groups of series, one of which approaches the lower limit $^2P_{1\frac{1}{2}}$, and the other of which approaches the upper limit $^2P_{\frac{1}{2}}$ (some 5000 and 9000 cm^{-1} away for Kr and Xe respectively). From six to eleven members each of some twenty or more series are found, from observed lines, to approach the lower limit $^2P_{1\frac{1}{2}}$, whereas only one or two members each of ten or more series approaching the upper limit $^2P_{1/2}$ are observed. The apparent reason is that succeeding members of these latter series lie above

the $^2P_{1\frac{1}{2}}$ limit. Electrons excited to any of these states are in the *continuum* of the lower set of levels having the same quantum numbers and parity, but approaching the lower limit. The result is, the ejection of an electron, (i.e. *auto-ionization*) and the return of the atom to the lower limit $^2P_{1\frac{1}{2}}$.

Three members of the $^3P^e$ (*3dmd*) series in calcium, made famous through the work of Russell and Saunders, lie above the series limit, $4^2S_{\frac{1}{2}}$, of the four chief series of singlets and triplets. The continuum above these four chief series corresponds to *even* S and D terms and to *odd* P and F terms. The *mean-life* of the three negative $^3P^0$ states is sufficiently great therefore to combine normally with lower *odd* terms and give respectable spectrum lines. The observed $^3S^3$ term, attributed to (*3d4d*) by Russell, in combination with other terms gives, as would be expected from a short mean-life, diffuse lines.

In strontium a negative $^3F^0$ term (*4d5p*) lies above the $5^2S_{\frac{1}{2}}$ limit and in a continuum of $^3F^0$ terms (*5s4f*). These negative $^3F^0$ (*4d6p*) terms, because they are observed at all, would be expected to have a very short *mean-life* and should therefore give rise to diffuse lines, as observed. These same $^3F^0$ terms in barium lie below the first limit $6^2S_{\frac{1}{2}}$ and give rise to sharp lines, as expected.

H. E. WHITE

Department of Physics,
University of California,
Berkeley, California,
September 9, 1931.

On the Range of Fast Electrons and Neutrons

Recent experiments on the stopping of cosmic rays raise again the question of the energy losses of electrons and protons with velocity very close to that of light. On the one hand we have a good deal of evidence that there are, associated with the cosmic rays, rays which are certainly not gamma-radiation, and which behave in some respects like beta-rays, since they produce a large number of ions in their passage through matter. This conclusion, which was reached originally by experiments with Geiger counters in series, has been beautifully confirmed by Mott-Smith,[1] who was able to show that the cosmic rays are accompanied by particles which produce definite cloud-chamber tracks, tracks rather thinner than those of an ordinary radioactive beta-particle. These ionizing rays are, according to Rossi, at least as penetrating as the cosmic rays themselves, and perhaps more so. On the other hand the independence of cosmic-ray intensities of terrestrial latitude makes it hard to believe that the rays enter the earth's atmosphere as charged particles. We should then want to know the theoretical answer to the question: Can a gamma-ray produce secondary beta-particles more penetrating than itself?

Numerous calculations have been made of the range of particles moving with velocities not too near that of light. Thus quantum-theoretical formulae have been obtained by Gaunt and Bethe, which in essential points confirm the classical formula of Bohr. But no quantum theoretical calculations have been made for particles of very high energy; and the classical result of Bohr for this case is based on a derivation which is not quite free from objection. Now it would seem at first that no adequate calculation could here be made, since we have at present no complete theory of the interaction of particles of very high relative velocity. That such a calculation is, nevertheless, possible rests on the fact that the processes chiefly responsible for the stopping of a beta-particle involve relatively insignificant energy losses, and that the mean energy loss of a beta-particle on collision with an atom is very small. This preponderance of relatively small energy losses becomes even more marked for particles whose velocity approaches that of light, and makes it possible to calculate the range of the particles without neglecting the retardation of the forces between them and the atomic electrons. Such a calculation has in fact been made by Møller for the collision of two free electrons; we have made it for the collision of electrons and protons with electrons bound in an atom. The results are very simple. If the energy of the particle (rest mass M, and charge E) is

$$\epsilon Mc^2$$

then for *very* large ϵ the number of ions produced per cm path increases with $\ln\epsilon$, and the energy loss per cm path through a gas in which there are N electrons per cc is

$$[4\pi e^2E^2N/mc^2]\cdot\ln\epsilon. \qquad (1)$$

[1] We want here to thank Dr. Mott-Smith for telling us at a Berkeley seminar of his recent very beautiful experiments.

Here e and m are the electronic charge and rest mass. For large but not very large ϵ this formula must be modified: to $\ln\epsilon$ must be added

$$\ln mc^2/k\hbar\nu$$

where m is the electronic rest mass, ν a mean ionization frequency for the atomic electrons, and $1.1 \leqq k \leqq 1.2$. This term is just the one found by Bethe for slow electrons, and in every case reduces the range of the particle below the value given by (2). The formula (1) gives for the range R of the particle

$$R = [mMc^4/4\pi e^2E^2N] \cdot [\epsilon/\ln\epsilon] \qquad (2)$$

This range is just twice that given by Bohr's relativistic formula. Our result gives equal ranges to electrons and protons of equal energy, and makes this range just one fourth of the mean distance, which, according to the Klein-Nishina formula, a gamma-ray of this same energy travels before its first Compton scattering.

The result (1) makes it hard to believe that the particles observed with cosmic rays are electrons or protons, since they are observed to ionize less than slower beta-particles. And if we believe in the approximate validity of the Klein-Nishina formula, then (2) shows that the particles cannot be secondary electrons. We have therefore thought it of interest to investigate the ionizing power of the neutrons, which were suggested by Pauli to salvage the theory of the nucleus. These neutrons,[2] it will be remembered, are particles of finite proper mass, carrying no charge, but having a small magnetic moment. Although the full calculations of the collision of such a neutron with an electron have not yet been completed, we have carried them far enough to see that there are characteristic differences between the ionizing power of a neutron and that of an electron, differences which rest ultimately upon the fact that the field of the neutron falls off more rapidly with distance than the Coulomb field. (The field of a neutron may, of course, be derived from its wave equation; and this has been given by Pauli.) In particular, the number of ions produced by a neutron is, for energies large compared to the electronic proper energy mc^2, sensibly independent of the velocity of the neutron, and of its mass, and does not increase, like (1), with increasing velocity. Thus even a very fast neutron would, if its magnetic moment were of the order of that of the proton, produce ion tracks perceptibly thinner than those of a beta-particle. It will be remembered that, according to Pauli, it is one of the functions of the neutron to carry off the apparently lost energy in a radioactive beta-ray disintegration. It would be of extreme interest to see whether, in such a disintegration, thin tracks, of the kind observed by Mott-Smith, could be found. If they were found, we should be certain that the neutrons not only played a part in the building of nuclei, but that they also formed the cosmic rays; if no such tracks were found, we should know that the neutrons, if they exist at all, have nothing to do with cosmic radiation.

The theory of the collision of neutrons and electrons, and the detailed calculation of the ranges of neutrons and fast electrons, will be published very shortly.

J. F. Carlson
J. R. Oppenheimer

LeConte Hall,
Berkeley, California,
October 9, 1931.

[2] We are much indebted to Dr. Pauli for telling us, at a theoretical seminar in Ann Arbor last summer, the elements of the theory of the neutron, its functions and its properties.

The Calculation of the Characteristic Frequency from the Coefficient of Compressibility

A number of years ago Einstein[1] derived an expression for the characteristic frequency of a monatomic solid which is as follows

$$\nu = 2.8 \times 10^7 A^{-1/3}\rho^{-1/6}\kappa^{-1/2} \qquad (1)$$

where κ is the coefficient of compressibility, A is the atomic weight and ρ is the density of the solid. This relation was derived from dimensional considerations, and the constant was evaluated by considering the effect on a given atom of its 26 immediate neighbors in a lattice which we now call the simple cubic or rock salt type. The result must be regarded as an approximation yet it is a useful one and therefore deserves further consideration. A reexamination of the derivation in the light of present knowledge reveals that several ambiguities and restrictions inherent in the original work now may be removed.

[1] Einstein, Ann. d. Physik **34**, 170 (1911); **35**, 879 (1911).

First, it would appear from the discussion as given by Einstein that it applies only to the lattice postulated and is limited by the number of neighboring atoms taken into account. This is not entirely true. A careful study of the calculations shows that the number of atoms considered may be cancelled out and need not appear in Eq. (2) of his second paper. This may be more easily seen if the generalized number n is substituted for 26. The only way the lattice enters into this result is through d, the equilibrium distance between atoms.

This brings us to the second point, namely, the device by which Einstein eliminates v, the atomic volume, in terms of d. This is accomplished by assuming that d is equal to the radius of a sphere of volume equivalent to that of 8 atoms, the number contained in the unit cube of the lattice he considered. A moment's reflection will show that this method does not give the true distance between the atoms, as recognized today but introduces a small error; hence some more exact and more general scheme of eliminating v is desirable.

The simplest way to do this is to express d, as determined by x-ray measurements, as an empirical function of v. This is easily done. In Fig. 1 values of d for a number of metals, as given by Ewald[2] are plotted against $(v)^{1/3}$ as calculated from the data of Vol. I of the International Critical Tables. The variation is linear and since elements possessing both face-centered and body-centered cubic structures are included the constant may be taken as identical for both systems without appreciable error. It may even be assumed as a first approximation that it holds for other types of lattice. The analytical expression for the curve of Fig. 1 is $d=1.35\times10^{-8}\ (v)^{1/3}$. By use of this in Eq. (2) of Einstein's second paper we get

$$\nu = 2.9 \times 10^{7} A^{-1/3}\rho^{-1/6}\kappa^{-1/2}. \qquad (2)$$

This is practically the same as the result given by him except that it is less restricted and may be safely given more general application.

It is interesting to note in this connection that if we give temperature the dimensions of energy, ml^2t^{-2}, as may be done[3] the coefficient of thermal expansion has the same dimensions as the coefficient of compressibility. This suggests that the expression

$$\nu = \text{const}\ A^{-1/3}\rho^{-1/6}\kappa^{-1/2} \qquad (3)$$

might yield useful information. A study of a number of metals shows that if the value 2.4×10^{8} is assigned to the constant, Eq. (3) leads to values of ν which are approximately correct except in the case of the alkali metals. This relation obviously has not the theoretical foundation which supports Eq. (1) since the symmetrical law of force assumed in the derivation of the latter leads to an expansion coefficient of zero. It is, however, an interesting empirical formula.

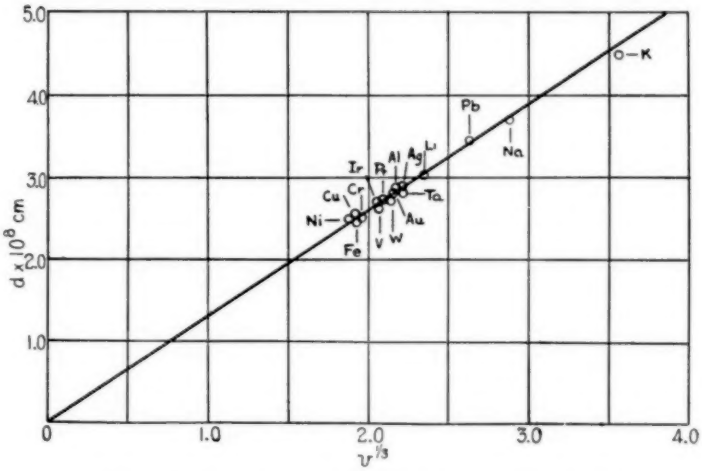

Fig. 1. The calculation of characteristic frequencies.

[2] Ewald, Handbuch der Physik, 24, Chap. 4. Springer, Berlin, 1927.

[3] Cf. Bridgman, Dimensional Analysis, Yale Univ. Press. 1922, p. 71.

TABLE I. *Comparison of values of ν for metals calculated by different methods.*

	Debye (Elastic constants)	Debye (Specific heat)	Grüneisen (Expans. coeff.)	Lindemann (Melting temp.)	Haber (Ultra-violet spectra)	Austin (Compressibility coeff.)	Austin (Expansion coeff.)
Ag	4.4	4.5	4.6	4.4	4.6	4.2	4.4
Al	8.3	8.3	7.7	7.8	8.2	7.0	8.1
Cd	3.5	3.5	3.7	2.8	—	2.8	3.5
Cu	6.8	6.6	7.1	6.8	7.2	6.0	6.0
Fe	9.7	9.5	8.5	8.3	—	7.0	7.5
Pb	1.5	1.8	2.2	1.9	2.5	2.1	1.8

In Table I values of ν for a few metals as calculated by Eqs. (2) and (3) are compared with those obtained by other methods as given by Rawlins and Taylor.[4] It will be observed that the agreement is satisfactory even in the case of cadmium, which possesses an hexagonal lattice.

J. B. AUSTIN

Research Laboratory,
U. S. Steel Corporation,
Kearny, N. J.,
October 7, 1931.

[4] Rawlins and Taylor, Infrared Analysis of Molecular Structure, Cambridge Univ. Press, Cambridge p. 86, 1929.

Crystalline Rubber Hydrocarbon

Substantially all of the chemical and physical evidence concerning the nature of rubber is consistent with the chemical formula $(C_5H_8)x$, and this is the generally accepted formula for "rubber hydrocarbon." An examination of the evidence discloses, however, that the above formula is not the only one which is consistent with this evidence. The difficulty of establishing beyond question the chemical composition of "rubber hydrocarbon" has been due largely to the lack of efficient physical methods for fractionating the "hydrocarbon," of proving that the final fractions are one-component systems, and of chemically identifying these fractions. If, as seems not improbable, "rubber hydrocarbon" is a mixture of closely related hydrocarbons not all of which can be represented by the formula $(C_5H_8)x$, no single method of fractionation can be relied upon to separate this mixture into its constituents. The only methods heretofore available for this purpose have been those based upon extraction with different liquids and fractional precipitation. One of the most powerful methods for fractionating a mixture of this character is systematic crystallization, and a laboratory technic for applying this method to "rubber hydrocarbon" has recently been developed at this Bureau. The conditions which must be met in order to induce crystallization in such a typically colloidal material as rubber can be predicted. These conditions have been met and are embodied in the following procedure.

The "rubber hydrocarbon," previously purified from all nonhydrocarbon materials, is dissolved to form a dilute solution in a suitable solvent. This solution is cooled to the temperature necessary to induce crystallization and then held at the desired temperature until crystallization is completed. The excess solution can then be removed and the crystals dried in vacuo for examination.

The accompanying photograph illustrates one type of crystal clusters which are obtained in this way. These crystals were grown at -55°C from a 0.05 percent solution of the hydrocarbon in pure dry ether.

The Bureau is now engaged in a determination of the melting point of these crystals, which point lies somewhere between -35 and 0°C. The melted crystals are typically rubber-like in nature, and a preliminary combustion analysis indicates a hydrogen-carbon atomic ratio close to 8/5, thus proving beyond any question that the crystals are rubber crystals. It is planned to carry out a systematic fractionation of "rubber hydrocarbon" by repeated crystallizations and to make accurate combustion analyses and molecular weight determinations of the final fractions.

This investigation has been carried out in the Section of Organic Chemistry of this Division under the direction of C. E. Waters.

The purification of the "rubber hydrocarbon" and the growing of the crystals were conducted by W. H. Smith, and the combustion analyses were made by H. J. Wing. The photomicrographic technic offered great difficulties, since the crystals had to be photographed in the solution at a temperature of −55°C. The development of this technic was started by F. W. Ashton and brought to successful completion by Charles P. Saylor.

In addition to the crystallization technic described above, it has also been found possible to distill the "rubber hydrocarbon," but fractionation by this procedure is very slow and of value only for confirmation purposes.

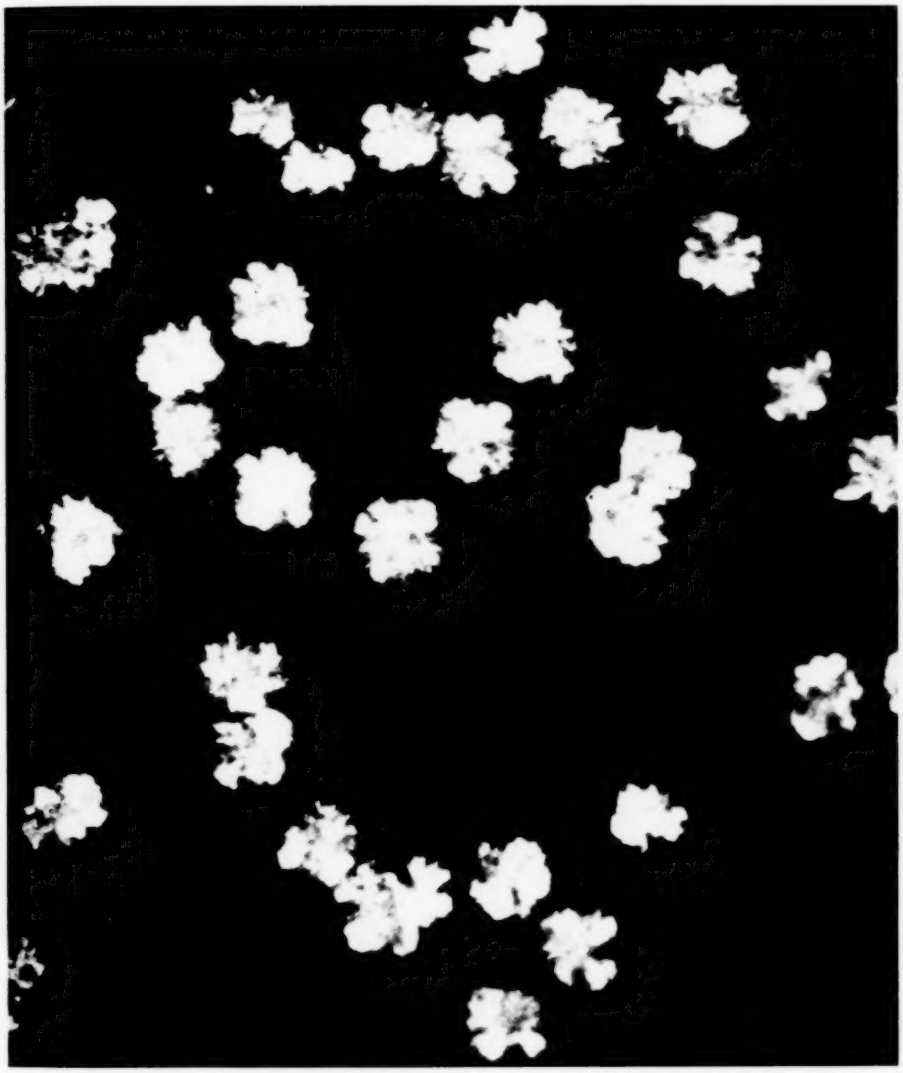

Fig. 1. Crystals of rubber hydrocarbon photographed between crossed nicols at a temperature of −55°C. Magnification—200 diams.

E. W. Washburn, Chief,
Chemistry Division
Bureau of Standards,
Washington, D. C.,
October 3, 1931.

Note on the Crystal Structure of Arsenic Triodide

In my paper (Phys. Rev. **38,** 351 (1931)) exact reference should have been made to correspondance between Dr. Braekken and myself (Zeits. f. Krist. **75,** 574 (1930)).

In Fig. 1, p. 355 "projection $\perp C$ axis" should have been a 60° rhombus and not a 60° parallelogram with unequal sides.

There are several misprints: T_{Th} should read T_{rh} in the abstract; parentheses are missing in the fifth line below Fig. 2 and $a°$ at the end of the ninth line below Fig. 2 should read A. In the "Discussion of the Structure" the distance of closest approach of iodine in layers perpendicular to the trigonal axis is given as "about 4.13A." There are really two interiodine distances in these planes, one a little smaller and one a little larger than 4.13A. Also in the final structure the iodine ions are not exactly in hexagonal close packing.

DOROTHY HEYWORTH

Ryerson Physical Laboratory,
Chicago, Illinois,
October 2, 1931.

Periodic System of Atomic Nuclei and the Principle of Regularity and Continuity of Series. A Correction

Since this paper [Phys. Rev. **38,** 1270 (1931)] was completed four new species have been found by Aston: Sr 11 (Fig. 9), Te 21 (Fig. 10), Ba 23 (Fig. 9), and Ba 25 (Fig. 10). The numbers given are the isotopic numbers. These species should be added to the known isotopes of Fig. 2. The first three are already listed as predicted by the principle of continuity and regularity of series in the figures of the given numbers. The fourth (Ba 25) belongs to the beryllium series and its existence is entirely in accord with the principle. Its existence points to the presence of a double level in the beryllium series at this point. The paper cites the earlier composition given for strontium and barium as "entirely inadequate."

WILLIAM D. HARKINS

Department of Chemistry,
University of Chicago,
October 3, 1931.

A New Criterion for Predissociation. A Correction

In a Letter to the Editor of the above title (Phys. Rev. **38,** 1079, 1931) line 14, the beginning of the sentence should read, "Transitions will occur not only" instead of "Transitions will not occur not only."

JOSEPH KAPLAN

University of California
at Los Angeles,
September 28, 1931.

BOOK REVIEWS

Periodisches System. EUGEN RABINOWITSCH AND DR. ERICH THILO. Pp. 302, Figs. 50. Verlag von Ferdinand Enke in Stuttgart, 1930.

A distinguished physicist once made a remark that all facts understood by chemistry belong to physics and that the mysteries left belong to chemistry. True or not, it must be admitted that wherever the carriage of chemistry got stuck, physics was generous enough to pull her out. In the book of Rabinowitsch and Thilo, published under the modest title "Periodic System" dealing with subjects on the border line between physics and chemistry, many modern and historical examples are given of the progress of chemistry by the advanced views in physics. The first fifty pages give a historical review of the history and development of the periodic system beginning with the fifteenth century B.C. It is interesting to note that the history of the basic unit weight of matter is not yet finished although the writers state (page 16) that, "das auf Sanerstoff gleich 16 basierend Atomgewichtssystem ist bis jetzt allgemein beibehalten." Recently after the discovery of the isotopes of oxygen, Aristide von Grosse (1930) proposed to refer the atomic weight to $He^4=4.000$; Aston (Nature 1931) on the other hand concludes that neither helium nor the proton, etc. are units free from objection!

Since the periodic properties of the atom have in recent times been so closely related to its structure, the authors appropriately devote Part II to the structure of the nucleus, Part III to the spectroscopic evidence for its electronic structure as developed by Bohr and later modified by the principles of wave mechanics, Part IV to a detailed consideration of the properties of each element and their relation to the position of each element in the periodic system. Finally, the fifth part of the book (fifty pages) deals with the periodicity of chemical properties and is of special importance to chemists. The possibility of existence of ionic (heteropolar) compounds is calculated from the heat of formation; the theory on the existence of atomic (homopolar) compounds cannot be presented in such a general form at the present time; the book, however, is stimulative to continued studies on this field.

Quite generally, it may be stated that the writers give a critical survey of our knowledge of the properties of the atom and they are quite honest in stating where the theories are not complete enough for a good understanding of all facts. This text can be recommended to any physicist or chemist interested in the development of the story of the atom and its importance for physics and chemistry. The book should be very useful in the hand of advanced students although it still would be more helpful to them if references to monographs and the literature had been made.

Print and appearance are excellent.

I. M. KOLTHOFF
University of Minnesota

Experimental Physical Chemistry. DANIELS, MATHEWS, AND WILLIAMS, Pp. 475, figs. 132. McGraw-Hill Publishing Company. New York, 1929. Price $3.50.

The book is divided into three parts. The first contains specific instructions for performing a large number of experiments; the second describes some of the standard apparatus of physical chemistry; the third describes some of the operations used in the practice. Altogether the amount of information compressed into the book is very great. It would seem to be both an excellent laboratory manual and a useful handbook for the more mature student.

In the first part are many experiments besides the classical ones of the older physical chemistry. The later chapters include experiments on radioactivity, photochemistry and electrochemistry of gases. Seventy-eight experiments in all are given; they cover so wide a field that if so large a number of experiments could actually be performed it would form an ideal background for the coming physical chemist. In fact, this can hardly be done in the usual elementary course; the book is the result of many years laboratory experience at the University of Wisconsin and there about half of the material embraced in the book is covered. The instruc-

tions are clear and each experiment is concluded with practical applications and suggestions for further work. The treatment is always interesting and suggestive.

The second part of the book covers a large field and though it cannot treat the various methods exhaustively it gives references which make it a suitable starting point for one looking up the technique in a not familiar field.

The book appears to be excellent as a laboratory manual and as a reference book it could well be on the shelf of any physical chemist or physicist. Much of the material is definitely physical and material is collected here which it is difficult to find elsewhere.

JOHN A. ELDRIDGE
University of Iowa

Electricity and Magnetism, an Advanced Textbook for Colleges. CHARLES A. CULVER, Macmillan Company, Publishers.

The book is based upon a three hour semester course which the author has given for junior and seniors in a College of Liberal Arts. The book takes up the fundamental principles from the usual point of view. By means of frequent tables of values and diagrams, frequent reference to recent work, and mention of apparatus used in current practice, the author keeps close to actual laboratory technique and gives the treatment of the theory a concreteness which it might not otherwise have possessed. It would seem an admirable text for a second course in electricity.

It is a notable fact that the names of Einstein and of Maxwell are not mentioned in the index. The first omission is not surprising since it is not yet customary to consider the close relation between electricity and the relativity theory even in quite advanced textbooks on electricity. It is rather more surprising that such a book could be written without referring to Clerk Maxwell.

JOHN A. ELDRIDGE
University of Iowa

Lehrbuch der Experimentalphysik für Studierende. DR. EMIL WARBURG, 21 and 22 Edition. Pp. 482, figs. 451. Theodore Steinkopff, Dresden and Leipzig, 1929. Price. Rm 15.80.

This is a textbook corresponding approximately to American first-year college texts. Judging by the large number of revised editions printed since the first edition in 1893, this book has been widely used.

O. M. STEWART
University of Missouri

Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren EUGEN WIGNER. Pp. 332, figs. 12. Friedr. Vieweg and Sohn Akt-Ges., Braunschweig, 1931. Price Rm 29.60.

"Dieses Buch ist aus dem Wunsche entstanden, die Anwendung gruppentheoretischer Methoden in der Quantenmechanik einem weiteren Leserkreis zugänglich zu machen."

Theoretical physicists seem to be pretty well divided into two camps, one of which has championed the theory of groups while the other has consistently refused to use it. As one physicist put it, papers on atomic structure can be divided into two classes—those which quote Schur and those which don't! This situation has been possible only because the results obtained from group theory in the problems of atomic structure have been largely duplicated and in some cases extended by use of more elementary methods. Coupling this with the fact that it is a real task to become in any sense familiar with the technique of group theory, it is small wonder that many do not consider the game worth the candle.

On the other hand, there are definite arguments to be advanced in favor of a wider study of the theory. While elementary methods can be used at present in atomic structure problems, the purely computational difficulties involved are becoming enormous. It seems that one must develop, if possible, some way of improving the starting point; i.e. the initial statement of the problem. How to do this is a question, but it does seem that group theory should be a good culture medium for the germs of thought on this problem because of the very power and generality of its methods.

Then too, one is well aware that the present quantum mechanics is no longer considered to be an adequate *general* theory of matter. Without attempting to be dogmatic, one may say that one of the most important advances which quantum mechanics has brought with it has been the emphasis on the symbolic method, as developed particularly by Dirac. While its real meaning seems by no means obvious, and while it is a double-edged tool to be used with caution, one can't help feeling that this symbolism really has great possibilities. Abstract group theory is, of course, a perfect example of the symbolic method, and one is encouraged to hope that the suggestiveness of its ideas will give valuable aid in the future development of a more correct quantum mechanics. On the basis of such ideas as these one can feel very favorably inclined towards a work such as this of Professor Wigner.

The first fifth of the book (62 pages) is devoted to preliminary material. Vectors and matrices in many dimensional complex space give the formal approach to the subject. The preliminary sections on the postulates of quantum mechanics, perturbation theory, and the statistical interpretation of quantum mechanics are naturally only brief reviews and summaries of these topics, but are ample for the purpose. Some may prefer to read these sections before the material on matrices in order to become oriented to Professor Wigner's style and viewpoint. The more elementary facts about abstract finite groups are developed in the next two sections—sub-groups, the separation of the elements into classes, the factor group, etc. The main theorems on the theory of representations of a group by matrices are contained in Secs. 9–12. Of particular interest is Sec. 10 on the treatment of continuous groups.

With Sec. 13 begins the problem of studying the groups of special interest to quantum mechanics—the symmetric (permutation) group and the group of rotations and reflections in three dimensional space. The last half of the book is devoted to the problems of atomic structure. Here one can find all of the important features of the *mathematical* theory. No attempt is made, of course, to include any experimental data. Attention may be called particularly to the treatment of the vector model and the development of the rules for the addition of vectors (p. 196).

The last section gives the group theory treatment of Slater's method for finding atomic wave functions. Developed originally by means of the most direct and elementary mathematical methods suited to the problem, one finds it here in a refined and spiritualized form.

The reviewer has found the treatment clear and precise throughout, but by no means always easy to follow. This is probably unavoidable since the subject matter is intrinsically difficult. The material is logically developed and shows evidence of great care in choice and arrangement. The printing has been done very carefully. The reviewer joins the author in expressing the hope that the book may help to diffuse knowledge of the theory among physicists.

E. L. Hill
University of Minnesota

Photochemical Processes, a General Discussion held by the Faraday Society. Pp. 573. Gurney and Jackson, London 1931. Price 10s 6d.

This report on photochemical processes, which is the fifty-fifth General Discussion of the Faraday Society, presents in a clear and interesting fashion the striking progress which has been made in this field since 1925. Its interest and value is considerably increased by the inclusion of the general discussions which followed all of the more important papers.

The first part of the report is devoted to a consideration of molecular spectra in relation to photochemical change. The subject is introduced with a clear and worthwhile review by R. Mecke, who also contributes a paper on the calculation of the ozone equilibrium in the atmosphere. The ultraviolet absorption spectra of acetylene and formaldehyde are discussed by G. Herzberg, and those of hydrogen sulfide, hydrogen selenide, and hydrogen telluride by C. F. Goodeve and N. O. Stein. The physical and chemical evidence in regard to the ultraviolet absorbtion of aldehyde and ketone vapors is reviewed by F. W. Kirkbride and R. G. W. Norish.

The second part, which is introduced by Max Bodenstein, consists of a series of papers on photochemical kinetics in gaseous systems. These papers deal chiefly with photochemical secondary processes; i.e., the chemical reactions which follow the initial excitation on dissociation.

The third part, which is devoted to photochemical changes in liquid and solid systems, is

introduced by A. Berthoud. In addition to several papers on photochemical reactions in liquid systems, there are in this group two papers on photographic processes and an interesting discussion of the temperature coefficient of photochemical reactions by K. W. Young and D. W. G. Style.

The fourth part, on Photosynthesis, is introduced by E. C. C. Baly, with a detailed account of some recent experiments on artificial photosynthesis. In addition to the papers on photosynthesis, this section includes a description, by Edith Weyde and W. Frankenburger, of a new actinometer for ultraviolet light.

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